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BACTERIAL CHEMOTHERAPY

IV. Synthesis of N^4, N^1-Diacyl Sulphanilamides*

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(*From the Haffkine Institute, Bombay*)

Received January 3, 1944

(Communicated by Lt.-Col. S. S. Sokhey, M.A., M.D., I.M.S., F.A.SC.)

That sulphanilamide acts by blocking the enzyme concerned in the utilisation of *para*-aminobenzoic acid (PAB), an "essential metabolite" in the bacterial cells of the susceptible organisms, by virtue of its structural resemblance to PAB, was first postulated by Fildes and Woods.[2,3] This concept has been extended,[4] in recent times, to cover the other well-known sulphonamides also: the varying potencies of the latter have been explained by the additional effect of the heterocyclic halves of their molecules on other metabolic processes peculiar to or more important to the particular bacterium under consideration.[5,6] In addition the hypothesis of Fildes and Woods receives its strongest support from the work of McIlwain and his collaborators, who by a study of the nutritional requirements of bacteria both in the presence and absence of antibacterial agents, were able to lay down successfully rules regarding structural specifications required for drug action in possible chemotherapeuticals.[7,8,9]

Despite the proved adequacy of the Fildes-Woods theory of the mechanism of action of the sulphonamides, yet another theory, namely, the Acidic Dissociation Theory has been recently formulated by Schmelkes[10] and Fox and Rose.[11] According to these authors, considering the present theory as only a slight elaboration of the original concept of Fildes and Woods and the non-specificity of sulphonamide action observed by other workers,[12] the sulphonamides act by virtue of the similarities of their ions $R\cdot S\langle^{O}_{O}-NH-$ to the $R\cdot C\langle^{O}_{O-}$ of PAB. They also state that the anions of the sulphonamide *acids*, rather than the cations or the undissociated acids, exert the bactericidal action. In support, they adduce evidence to show that the minimal amount of each drug (ionised drug) needed for bacteriostasis is approximately the same, irrespective of the test organisms used.

* A preliminary note on a few compounds reported in this communication appeared in *Current Science*.[1]

Although the acidic dissociation theory appears to open up new aspects of chemotherapeutical possibilities, exceptions can be taken to the theory in its present form. For instance, the hypothesis is founded on the classical conception of acids and consequently lays emphasis on acidic dissociation of the sulphonamides as an essential prerequisite for the antibacterial activity of the latter. On this basis it is difficult to explain the activity of the sulphonamides in which both the hydrogen atoms at the $—SO_2.NH_2$ have been substituted and which in all probability are unlikely to give rise *in vivo* to ionisable derivatives: examples of this class of compounds are the sulphanilyl derivatives of dimethyl amine,[13,14] diethylamine,[13] diethanolamine[15,16] and, of the α-pyridyl, α-thiazolyl and α-thiazolinyl methylamines.[17] In contrast to the Fildes-Woods theory which is based on the structural specificity of the sulphonamide types, the acidic dissociation theory maintains that the heterocyclic halves of the sulphonamides contribute only to a greater capacity of the molecules for acidic dissociation. However, conception of the sulphonamides as acids in the more comprehensive, modern sense, postulated by Brönsted[18] and Lowry,[19] helps to remove the above and other apparent anomalies in the acidic dissociation theory which, it will be remembered, arise from the interpretation of acids in the classical restricted sense by the sponsors of the theory.

The acidic dissociation theory suggests the possibility that if sulphonamides could be rendered more " acidic " by suitable means more potent chemotherapeuticals than those hitherto available could be obtained. It also raises the question whether by transformation of the sulphanilamide molecule itself compounds of the same acidity and the same degree of activity as the most powerful sulphonamides now known cannot be prepared. It appeared that these objects could be achieved by the incorporation of acyl radicals at the sulphonamide part of the molecule instead of the more difficult task of introducing heterocyclic ring systems at the N^1-position of sulphanilamide. A search of the literature reveals that many compounds of the N^1-acyl sulphanilamide type have already been disclosed.[16,28] Although they have not been investigated at length with the exception of " albucid ", many of the straight chain derivatives and the N^1-isocyclicacyl sulphanilamides are stated to be, weight for weight, as good as sulphanilamide in experimental streptococcal infections. On an equimolecular basis, these derivatives—some contain less than fifty per cent. of sulphanilamide—were definitely superior to sulphanilamide. These results are parallel to those obtained with some the higher straight chain N^4-acyl sulphonamides,[20] which include a few therapeutically valuable members.[21] The case of albucid is remarkable: recent studies[22] have revealed it to possess not only a low order of toxicity

but also effectiveness, at least in some infections, in even sulphathiazole-resistant cases. Interesting data of a far-reaching nature may therefore be expected to accrue by a detailed study of members of the N^1-acyl sulphanilamide group and by attempting correlation of the degree of dissociation of the N^1-acyl sulphanilamides with their activity in experimental infections.

The author's interest in the N^4-, N^1-diacyl sulphanilamides was stimulated by the earlier attempt[23] to render the sulphonamides mycobactericidal by the further introduction of fatty acid groupings in their molecules. The present communication deals with the synthesis of a series of N^4, N^1-diacyl derivatives of sulphanilamide which are listed in the table.

Serial No.	Name	M.P./°C.	Nitrogen percentage	
			Found	Required
42	N^4-*n*, Caproyl, N^1-acetyl sulphanilamide ..	166–69 dec.	8·8	9·0
43	N^4-*n*, Caproyl, N^1-*n*, butyryl sulphanilamide ..	164–68	8·2	8·2
44	N^4, N^1-Di (*n*, caproyl) sulphanilamide ..	164–72	7·9	7·6
45	N^4-*n*, Caproyl, N^1-*n*, heptoyl sulphanilamide ..	148–52	7·7	7·3
46	N^4-*n*, Caproyl, N^1-palmityl sulphanilamide ..	123–26	5·6	5·5
47	N^4-*n*, Caproyl, N^1-stearyl sulphanilamide ..	127–30	5·0	5·2
48	N^4, N^1-Di (*n*, butyryl-) sulphanilamide ..	217–20	8·7	9·0
49	N^4, N^1-Di (*n*, heptoyl-) sulphanilamide ..	131–34	7·6	7·1
50	N^4-*n*, Caproyl, N^1-benzoylsulphanilamide ..	180–83	8·0	7·5
51	N^4-*n*, Caproyl, N^1-cyclohexoylsulphanilamide ..	185–87	7·3	7·3
52	N^4-*n*, Capryol, N^1-cinnamoyl sulphanilamide ..	228–31	7·1	7·0
53	N^4-*n*, Caproyl, N^1-(*a*, naphthoyl-) sulphanilamide	154–57	6·8	6·5
54	N^4-*n*, Caproyl, N^1-(*m*, nitrobenzoyl-) sulphanilamide	173–78	10·1	10·4
55	N^4-*n*, Caproyl, N^1-(*p*, nitrobenzoyl-) sulphanilamide	222–30	10·0	10·4
56	N^4, N^1-Dibenzoyl sulphanilamide	239–40	..	..
57	N^4, N^1-Dicyclohexoyl sulphanilamide	248–50	7·0	7·1
58	N^4, N^1-Dicinnamoyl sulphanilamide	216–18	6·8	6·5
59	N^4, N^1-Di (*p*-nitrobenzoyl-) sulphanilamide ..	251 dec.	11·7	11·9
60	N^4, N^1-Difuroyl sulphanilamide	255 dec.	7·8	7·7
72	N^4, N^1-Di (*p*-nitrobenzoyl-) sulphapyridine ..	232–34 dec.	13·0	12·9

From the standpoint of both the acidic dissociation and the Fildes-Woods theories, the presence of the grouping $H_2N\cdot C_6H_4\cdot SO_2\cdot NH$ in the sulphonamide molecules is considered to be of fundamental physiological significance.[3,5,10,24,25] A stable structural alteration in this unit has been observed to be accompanied by a destruction of therapeutic activity and is comprehensible in the light of the finding that similar permanent alterations in the molecule of PAB depress or nullify[3,22] the growth-promoting action of PAB.[37] The synthesis of N^4, N^1-diacyl sulphanilamides may, perhaps, be considered as unproductive of interesting results on the ground that the significant, free amino group is not present in their molecules.

It may, therefore, be well, at this stage, to state the theoretical considerations for undertaking the synthesis of N^4, N^1-diacyl sulphanilamides. In the synthesis of this type of compounds, in addition to the possibility of their proving mycobactericidal, a primary consideration was the relative ease with which they could be prepared as compared to the strictly N^1-acyl derivatives of sulphanilamide. Considering the smoothness with which some of the N^4-acyclic acyl sulphanilamides are cleaved to sulphanilamide[24,27] and the facility with which the N^4-acyl group is split off from N^4, N^1-diacyl sulphanilamides,[28] the N^4-acyclic acyl, N^1-substituted sulphanilamides (Nos. 42–55) will, in all probability, give rise *in vivo* to the respective N^1-acyl sulphanilamides. It was, therefore, of particular interest to ascertain whether or not the observed therapeutic effect of this class of compounds may not after all be that of the N^1-acyl sulphanilamides themselves, modified or otherwise by the presence of the fatty acids simultaneously liberated. Such an enquiry was expected to lead to a study of the detoxication mechanisms involved in the passage of the active members through the animal body both in a state of health and disease. Again, the synthesis of the N^4, N^1-isocyclic acyl sulphanilamides (Nos. 56–72) needs explanation. It is true that the lack of activity of the N^4-isocyclic or heterocyclic acyl sulphonamides, hitherto reported, is generally understood to bedue to the inability of experimental animals to hydrolyse aroyl or heteroöyl amide linkages.[16] Nevertheless, there are a few instances of this kind of N^4-substituted sulphanilamides, for example, N^4-furoyl sulphapyridine[29] and the N^4-nicotinyl,[16,29,30] N^4-quinolinyl,[31] and N^4-(5, pyrrolidone-2, carbonyl-[32]) and the N^1, 4′-(*p*-anisylidene-) or the N^1, 4′-(*p*-dimethylaminobenzylidene-) aminophenyl, N^4- acetyl sulphanilamides,[16] whose activity is consequently surprising and has not yet been plausibly explained. In the contemplation of the synthesis of the N^4, N^1-diisocyclic acyl sulphanilamides, it was encouraging to find that a further substitution of the acyl group at the sulphonamide portion, even though exemplified so far in the isolated case of N^4, N^1-dibenzoyl sulphanilamide,[33] is sufficient to render active an otherwise inert N^4-acyl sulphanilamide.[34] Unfortunately, an explanation for the activity of dibenzoyl sulphanilamide founded on experimental data has not yet been offered by the original investigators. Such an explanation would no doubt have a important bearing on the Fildes-Woods theory of sulphonamide action which lays emphasis on the role of a free or potential amino group in conditioning the physiological action of the sulphonamides. A study of the compounds, Nos. 56–72 was, for obvious reasons, expected to answer ultimately the question of whether or not the activity of N^4, N^1-dibenzoyl sulphanilamide is the consequence of an inherent characteristic of this type

of compounds. The case of the *p*-nitrobenzoyl derivatives (Nos. 55, 59, 72) deserves mention. Judging from analogy,[35] they are to be expected to be reduced *in vivo* to the corresponding amino bodies; these latter, besides probably fulfilling the requisites for high anionic dissociation, would then represent compounds bearing a structural resemblance to the bacterial "essential metabolite", PAB different from the type obtaining in other sulphonamides.

Whether any or all of the expectations of this study will be realised can be settled only by actual biological trials. It is however reasonable to hope that even if no highly antibacterial agents are encountered in the group of compounds now synthesised, the present study would be atleast instrumental in shedding additional and useful light on the existing theories* of the mechanism of action of the sulphonamides.

Experimental

For the N^4-*n*, caproyl, N^1-substituted derivatives (Nos. 42, 43, 45, 46, 47, 50–55) of sulphanilamide, N^4-*n*, caproyl sulphanilamide — reported[34] to be as antistreptococcal as sulphanilamide itself, but much less toxic— constituted the starting material: the condensations with the desired acid chlorides were carried out in pyridine medium. The remaining N^4, N^1-diacyl sulphanilamides (Nos. 44, 48, 49, 56–60) resulted directly by the operation of slightly more than 2 mols. of the appropriate acid chlorides on sulphanilamide itself in pyridine solution.

The condensation products, obtained by dilution of the reaction mixtures with excess of water, were severally purified usually through precipitation from their dilute sodium hydroxide solutions (charcoal) by acidification. They were mostly recrystallised from alcohol, the exceptions being Nos. 53, 56, 57 and 60 which were crystallised from acetone and No. 59 which was obtained from nitrobenzene. All these compounds (Nos. 42–60) were obtained as colourless needles.

The disubstituted pyridine derivative (No. 72) was prepared by similar action of 2 mols. of *p*-nitrobenzoyl chloride on sulphapyridine in the presence of pyridine. It separated from acetone as colourless plates.

The yields of the compounds reported in this paper were, in all instances, good.

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* While this MS. was under preparation, there has appeared an interesting paper by Bell and Roblin,[36] admirably correlating ionic dissociation with activities of the sulphonamide types.

The melting points of many of the compounds listed are not at all sharp in spite of their many recrystallisations and homogeneous crystalline structure: this appears to be an inherent characteristic, as has previously been observed[28] in the case of the N^1-acyl sulphanilamide derivatives.

I desire to take this opportunity of expressing my indebtedness to Col. S. S. Sokhey but for whose kind interest and encouragement this investigation would not have been possible. I am also thankful to the Lady Tata Memorial Trust for the award of a Scholarship.

Summary

With the object of exploring the group of N^4, N^1-diacyl sulphanilamides for practicable antibacterial agents and in view of the possibility of shedding further light on the existing theories of the mode of sulphonamide action by a study of the N^4, N^1-diacyl sulphanilamide type of compounds, a number of N^4, N^1-diacyl sulphanilamides, twenty in all, have so far been synthesised.

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BACTERIAL CHEMOTHERAPY

V. Synthesis of Phenolic Azo-dyes derived from the Sulphonamides

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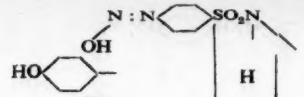
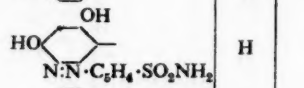
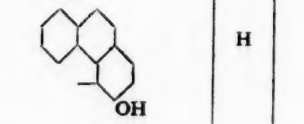
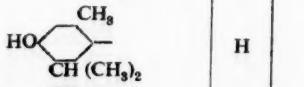
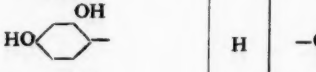
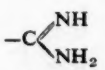
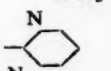
THE effective chemotherapy of many bacterial infections with the sulphonamide group of drugs which has been possible in recent times owes its origin to the introduction of an azo-dye, *prontosil* in clinical practice by Domagk.[1] While very different explanations for the ways in which the various azo-dyes in therapeutic use[2,3] exert their antiseptic action have been advanced, opinion[4] concerning the mode of action of the azo-dyes derived from the sulphonamides, of which prontosil is one, is at the present time almost unanimous. Although by no means fully proved, it is generally believed that the therapeutic properties of the sulphonamido azo-dyes are primarily the therapeutic properties of the sulphanilamide itself, which has resulted from reductive cleavage of the azo-linkage *in vivo* and this explains, to a great extent, the increasing disuse of the prontosil types in the treatment of acute bacterial infections.

It should be remembered that in addition to the sulphonamides resulting from these azo-dyes, amino phenols or aromatic polyamines are also at the same time liberated by the *in vivo* cleavage at the azo double bonds. It is, therefore, of interest to enquire whether or not the latter contribute in any manner to the observed final physiological effect. Previous knowledge of biological oxidations and the detoxication mechanisms of amino phenols, aromatic polyamines and the anti-hæmorhagic compounds[5] would suggest the possibility of production *in vivo* of quinonoid bodies from the "second ring" not bearing the sulphonamido group. This assumes great interest because many natural and synthetic quinones have recently come to be recognised as powerful antibacterial agents[6] and many quinones, in addition to their occurrence[7] in some bacteria, are known to constitute essential growth factors[8] for many types of bacteria. Furthermore, the observed influence of other compounds on the detoxication of the sulphonamides themselves[9,10,11,12] and the phenomenon of synergism of action of the sulphonamides

and azochloramide,[13] urea[14] or some purines,[15] which is finding increasing application in actual practice, would appear to have a bearing on enquiries directed towards the mode of action of the sulphonamido azo-dyes. Such enquiries would appear to be somewhat justified in view of past literature on the sulphonamido Schiff's bases; the Schiff's bases derived from the sulphonamides are hydrolysed, after oral administration, into the component parts; the possibility of the "aldehyde half" of the molecule or its derivative elaborated *in vivo* exerting a modifying influence on the chemotherapeutic efficacy of the active half has already been indicated in an earlier paper.[16] That the second ring in azo-dyes may well be of significance was indicated by Gley and Girard's finding[17] that whereas molecular equivalents of prontosil and sulphanilamide were of equal therapeutic value in experimental streptococcal infections, the carboxy derivative of prontosil, which could liberate no more sulphanilamide than prontosil, was twice as effective, therapeutically, as prontosil. The possibility envisaged by Gley and Girard may be construed to receive support from the activities reported for the azo-dyes derived from sulphanilamide and resorcinol,[18] 3 : 5-diaminobenzoic acid,[19] *p*-hydroxy phenyl glycine and histidine,[20] pyrrole and indole[21] and some purines[22]; prontosil and neoprontosil may also probably be included in this group.

A scrutiny of the existing literature on the sulphonamido azo-dyes brings to light many curious generalities. For instance, while quite a considerable number of dyes derived from sulphanilamide itself is known, a comparatively smaller number of their heterocyclic analogues has been disclosed. Again, as against the basic dyes, very few phenolic dyes have, so far, been revealed. Furthermore, only a small proportion of either the basic or acidic dyes have been studied in detail in respect of their activity and their detoxication mechanisms. That a study of the sulphonamido azo-dyes need not be considered entirely fruitless is supported by the use of other dyes still in medicine and the notable success achieved recently[23] by Congo red in even the sulphonamide-resistant bacterial infections.

For the reasons stated above, it was therefore, considered worthwhile to synthesise a series of azo-dyes derived on the one hand, from sulphonamides which have already earned a definite place in chemotherapy and on the other, from mono- and poly- hydric phenolic compounds. In the hope that useful information likely to lead to a better understanding of the evolution of future chemotherapeuticals could be gained, it was further planned to investigate first their usefulness in experimental bacterial infections and later, the mechanism of action of the active members. The phenolic dyes which were prepared in this connection are represented in the table.

Serial No.	Name				Nitrogen percentage	
					Found	Required
99	2 : 4-Dihydroxy, (*p*-sulphamyl phenyl azo-) benzene		H	H	13·8	14·3
100	2 : 4-Dihydroxy, 1 : 5-*bis* (*p*-sulphamyl phenyl azo-) benzene		H	H	17·4	17·7
101	4-Hydroxy, (*p*-sulphamyl phenyl azo-) naphthalene		H	H	12·3	12·8
102	3-Hydroxy, 4 (*p*-sulphamyl phenyl azo-) phenanthrene		H	H	11·3	11·1
103	2-Methyl, 4-hydroxy, 5-*iso*propyl, (*p*-sulphamyl phenyl azo-) benzene		H	H	11·9	12·6
104	2 : 3 : 4-Trihydroxy, (*p*-sulphamyl phenyl azo-) benzene		H	H	13·1	13·6
105	2 : 4-dihydroxy, (*p*-sulphonguanidyl phenyl azo-) benzene		H		21·0	20·9
106	2 : 4-Dihydroxy, (*p*-N^1, 2′-pyridyl sulphamyl phenyl azo-) benzene		H		14·8	15·1
107	2 : 4-Dihydroxy, (*p*-N^1, 2′-thiazolyl phenyl azo-) benzene		H		14·6	14·8
108	2 : 4-Dihydroxy, (*p*-N^1, 2′-thiazolinyl sulphamyl phenyl azo-) benzene		H		14·3	14·8
109	2 : 4-Dihydroxy, 5 (*p*-N^1, 2′-thiazolyl sulphamyl phenyl azo-) quinoline		H		16·4	17·0

Two compounds listed in the table have previously been reported but in insufficient detail and were therefore included with the object of a comparative and detailed study in animal experiments: the compounds are No. 99[18] and No. 103.[24] Four of the dyes (Nos. 106–109) have, so far, been subjected by Dr. B. B. Dikshit to preliminary tests in experimental *Pasteurella pestis* infections in mice. Although the results obtained were somewhat interesting, none of them exhibited an activity greater than that of sulphathiazole, the control used in comparative bio-assays of the efficacies of new sulphanilamide derivatives in this Institute.

Experimental

The *dyes, Nos. 99-104, 106-109* were all prepared by the following general procedure which is illustrated by the preparation of the *compound, No. 99*. A solution of sulphanilamide (17·2 g., 1 mol.) in sodium hydroxide (4 g. in 100 c.c. of water), cooled to 15°, was treated with a solution of sodium nitrite (7·4 g. in 20 c.c. of water; 1·08 mol.) and the resulting solution poured with stirring on to a mixture of concentrated hydrochloric acid (21·2 c.c. of D, 1·18; 2·5 mols.) and crushed ice (120 g.). The diazonium salt mixture, after standing 15–20 minutes, was then added with good stirring to a solution of resorcinol (11 g., 1 mol.) in sodium hydroxide (20 g. in 80 c.c. of water; 5 mols.) which had previously been cooled to about 0–5° C. by addition of ice (80 g.). The resulting solution was allowed to stand at ordinary temperature for one half hour, filtered and acidified with hydrochloric acid when the dye separated out as a voluminous precipitate.

For the *compound, No. 105*, a slightly different process was adopted. This consisted in the direct diazotisation of a dilute hydrochloric acid solution of sulphaguanidine itself by means of sodium nitrite followed by coupling with resorcinol in alkaline medium on the same lines as has been worked out for the other azo-dyes.

The attempts to crystallise the dyes from the usual organic solvents or mixtures of them did not meet with success. Resort was therefore had, for purposes of purification, to repeated fractional precipitation of the dyes from their aqueous alkaline solutions (Norite) by acetic acid, the first and final fractions being rejected. The dyes after washing with water and drying in an air-oven, were then obtained as powders without any definite melting points or crystalline natures but possessing one or other grades of redness.

The yields of the pure dye-stuffs should, in all the instances, be considered good since they average from 75–90 per cent. of the theoretical.

The author wishes to express his gratefulness to Col. S. S. Sokhey for his kind interest in this investigation and to the Lady Tata Memorial Trust for the award of a Research Scholarship.

Summary

The synthesis of a series of phenolic azo-dyes derived from the sulphonamides with the object of exploring their therapeutic potentialities and of gaining an insight into their mode of action, has been effected and reported.

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CALCULATION OF THE ELASTIC CONSTANTS OF QUARTZ AT ROOM TEMPERATURE FROM THE RAMAN EFFECT DATA

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1. Introduction

The elastic constants of a crystal can be calculated if the various force-constants in the crystal are known. When a crystal is subjected to a homogeneous strain, the various bond distances and the bond angles in the unit cell of the crystal get altered, and these can be calculated on the basis of the known crystal structure. By assuming the force-constants for the changes along valence bonds and angular deformations, the energy per unit volume due to the strain can be calculated. As this energy is known in terms of the elastic constants, the latter can be expressed in terms of the force-constants. These force-constants can be calculated from the Raman and infra-red data, and thus we get a method of calculating the elastic constants of the crystal directly from the spectroscopic observations. Both the elastic deformations and infra-red vibrations take place sufficiently slowly for the electronic cloud of atoms to adjust themselves to altered conditions. Whatever changes may take place are therefore fully taken care of in any scheme of force-constants which fits the infra-red data, and same scheme should therefore also fit the elastic constants.

In the present paper the elastic constants of α-quartz have been calculated on the basis of the ideas set forth above. The crystal structure of α-quartz is known from the X-ray studies of Gibbs[1] (1925), and the force constants in the crystal can be calculated on the basis of the group theoretical analysis of the Raman and infra-red spectra of α-quartz made by the author[2] (1940). The four force-constants which have been calculated from the Raman effect data are those of Si—O valence, Si$\diagup^{O}\diagdown$Si and O$\diagup^{Si}\diagdown$O

deformation, and O—O repulsion, and these explain the elastic constants as well.

2. *Calculation of the Variations of the Bond Distances and Bond Angles due to Strain*

When a crystal is subjected to homogeneous strain we may assume the strain to consist of two parts—the one involving displacements of partial lattices relative to each other and a second part in which the distance from basis to basis is altered as if the basis were rigid and attached at one point in the continuum subjected to strain. The high frequencies of vibration observed spectroscopically and also the structure of the crystal shows that quartz is not an ionic crystal. The silicon-oxygen bonds are largely covalent in nature. For this reason the piezo-electric forces produced by the strain are not likely to effect the elastic constants to any marked extent, and we may therefore treat the strain from the continuum stand point alone. But in the covalent binding between dissimilar atoms there would be a certain displacement of electric charges which would explain the piezo-electric behaviour of the crystal.

In any homogeneous pure strain, if x, y, z be the co-ordinates of a point in a body before it is strained and if $x + u$, $y + v$, $z + w$ be the co-ordinates of the same point after the body has been strained then we have (Love, *vide* ref. 3).

$$u = u_{xx} \cdot x + \tfrac{1}{2} u_{xy} \cdot y + \tfrac{1}{2} u_{xz} \cdot z$$

$$v = \tfrac{1}{2} u_{yz} \cdot x + u_{yy} \cdot y + \tfrac{1}{2} u_{yz} \cdot z$$

$$w = \tfrac{1}{2} u_{zz} \cdot x + \tfrac{1}{2} u_{zy} \cdot y + u_{zz} \cdot z$$

where u_{xx}, u_{yy}, u_{zz} represent the strain components parallel to x, y, z axes and u_{yz}, u_{xz}, u_{xy} represent components of shear in the yz, xz and xy planes. The strain may be regarded as a symmetrical tensor so that $u_{sr} = u_{rs}$. If P and Q be two points x_1, y_1, z_1 and x_2, y_2, z_2 and if r be the distance between them and l, m, n the direction cosines of the line PQ then the change in the length of PQ after deformation is given by

$$r\,(u_{xx} \cdot l^2 + u_{yy} \cdot m^2 + u_{zz} \cdot n^2 + u_{xy} l \cdot m + u_{yz} mn + u_{zx} ln)$$

$$= \frac{1}{r} [\Sigma\, u_{xx} \cdot (x_1 - x_2)^2 + \Sigma\, (y_1 - y_2)\,(x_1 - x_2)\, u_{xy}].$$

The unit cell of α-quartz is shown in Fig. 1. Atoms 1 to 6 are silicon atoms and atoms 7 to 12 are oxygen atoms contained in the unit cell while the remaining marked ones are oxygen atoms not contained in the unit cell but linked to silicon atoms 1 to 6 of the unit cell. The co-ordinates of the atoms in the unit cell were given by the author[4] (1942) while the co-ordinates

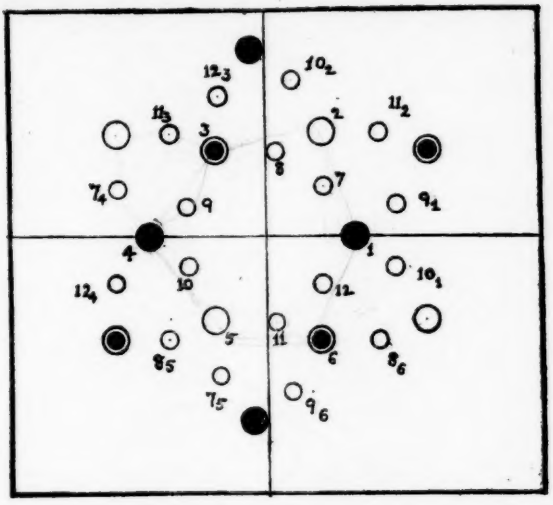

FIG. 1. Projection of Si & O atoms on the basal plane

of the remaining oxygen atoms such as 9_1 and 9_6 linked to silicon atoms 1 and 6 respectively can be obtained from those of oxygen atom 9 by moving this atom through a distance equal to 4·879 parallel to the lines joining Si atoms (1 and 4) and (3 and 6) respectively. The co-ordinates are given in Table I.

TABLE I

Atoms contained in the unit cell				Atoms not contained in the unit cell			
Atom number	x	y	z	Atom number	x	y	z
8—O	·3322	1·853	−2·966	9_1—O	3·1082	·6389	1·168
2—Si	1·318	2·282	−1·798	10_1—O	3·1082	— ·6389	−1·168
7—O	1·4386	1·214	— ·63	8_6—O	2·7717	−2·3722	2·428
1—Si	2·244	0	0	9_6—O	·6687	−3·5863	1·168
12—O	1·4386	−1·214	·63	7_5—O	−1·0009	−3·0112	— ·63
6—Si	1·318	−2·282	1·798	8_5—O	−2·1073	−2·3722	−2·966
11—O	·3322	−1·853	−2·428	12_4—O	−3·4404	−1·214	·63
5—Si	−1·122	−1·944	−1·798	7_4—O	−3·4404	1·214	— ·63
10—O	−1·7708	— ·6389	−1·168	11_3—O	−2·1073	2·3722	2·966
4—Si	−2·635	0	0	12_3—O	−1·0009	3·0112	·63
9—O	−1·7708	·6389	1·168	10_2—O	·6687	3·5863	−1·168
3—Si	−1·122	1·944	1·798	11_2—O	2·7717	2·3722	−2·428

The variations (Δr_i) of the Si − O distances are given by

$$\Delta r_{1,7} = \frac{1}{1\cdot588}\,[\,\cdot6486\,u_{xx}+1\cdot474\,u_{yy}+\cdot397\,u_{zz}-\cdot9777\,u_{xy}-\cdot7647\,u_{yz}+\cdot5074\,u_{zx}]$$

$$\Delta r_{1,12} = \frac{1}{1\cdot588}\,[\,\cdot6486\,u_{xx}+1\cdot474\,u_{yy}+\cdot397\,u_{zz}+\cdot9777\,u_{xy}-\cdot7647\,u_{yz}-\cdot5074\,u_{zx}]$$

$$\Delta r_{2,7} = \frac{1}{1\cdot588}\,[\,\cdot0155\,u_{xx}+1\cdot141\,u_{yy}+1\cdot364\,u_{zz}-\cdot1288\,u_{xy}-1\cdot248\,u_{yz}+\cdot1408\,u_{zx}]$$

$$\Delta r_{6,12} = \frac{1}{1\cdot588}\,[\,\cdot0155\,u_{xx}+1\cdot141\,u_{yy}+1\cdot364\,u_{zz}+\cdot1288\,u_{xy}-1\cdot248\,u_{yz}-\cdot1408\,u_{zx}]$$

$$\Delta r_{2,8} = \frac{1}{1\cdot588}\,[\,\cdot972\,u_{xx}+\cdot1840\,u_{yy}+1\cdot364\,u_{zz}+\cdot4239\,u_{xy}+\cdot5010\,u_{yz}+1\cdot152\,u_{zx}]$$

$$\Delta r_{6,11} = \frac{1}{1\cdot588}\,[\,\cdot972\,u_{xx}+\cdot1840\,u_{yy}+1\cdot364\,u_{zz}-\cdot4239\,u_{xy}+\cdot5010\,u_{yz}-1\cdot152\,u_{zx}]$$

$$\Delta r_{4,9} = \frac{1}{1\cdot588}\,[\,\cdot7468\,u_{xx}+\cdot4081\,u_{yy}+1\cdot364\,u_{zz}+\cdot5521\,u_{xy}+\cdot7461\,u_{yz}+1\cdot009\,u_{zx}]$$

$$\Delta r_{4,10} = \frac{1}{1\cdot588}\,[\,\cdot7468\,u_{xx}+\cdot4081\,u_{yy}+1\cdot364\,u_{zz}-\cdot5521\,u_{xy}+\cdot7461\,u_{yz}-1\cdot009\,u_{zx}]$$

$$\Delta r_{3,9} = \frac{1}{1\cdot588}\,[\,\cdot4209\,u_{xx}+1\cdot703\,u_{yy}+\cdot397\,u_{zz}+\cdot8465\,u_{xy}+\cdot8219\,u_{yz}+\cdot4087\,u_{zx}]$$

$$\Delta r_{5,10} = \frac{1}{1\cdot588}\,[\,\cdot4209\,u_{xx}+1\cdot703\,u_{yy}+\cdot397\,u_{zz}-\cdot8465\,u_{xy}+\cdot8219\,u_{yz}-\cdot4087\,u_{zx}]$$

$$\Delta r_{3,8} = \frac{1}{1\cdot588}\,[2\cdot115\,u_{xx}+\cdot00686\,u_{yy}+\cdot397\,u_{zz}-\cdot1323\,u_{xy}-\cdot0573\,u_{yz}+\cdot9160\,u_{zx}]$$

$$\Delta r_{5,11} = \frac{1}{1\cdot588}\,[2\cdot115\,u_{xx}+\cdot00686\,u_{yy}+\cdot397\,u_{zz}+\cdot1323\,u_{xy}-\cdot0573\,u_{yz}-\cdot9160\,u_{zx}]$$

The variations ($\Delta\Phi_i$) of Si$\overset{O}{\diagdown}$Si angles are given by

$$1\cdot355\,\Delta\Phi_{1,7,2} = -\cdot3645\,u_{xx}+\cdot389\,u_{yy}-\cdot013\,u_{zz}-\cdot074\,u_{xy}-\cdot394\,u_{yz}+\cdot47\,u_{zx}$$

$$1\cdot355\,\Delta\Phi_{1,12,6} = -\cdot3645\,u_{xx}+\cdot389\,u_{yy}-\cdot013\,u_{zz}+\cdot074\,u_{xy}-\cdot394\,u_{yz}-\cdot47\,u_{zx}$$

$$1\cdot355\,\Delta\Phi_{3,9,4} = \cdot137\,u_{xx}-\cdot11\,u_{yy}-\cdot013\,u_{zz}+\cdot365\,u_{xy}+\cdot607\,u_{yz}+\cdot108\,u_{zx}$$

$$1\cdot355\,\Delta\Phi_{4,10,5} = \cdot137\,u_{xx}-\cdot11\,u_{yy}-\cdot013\,u_{zz}-\cdot365\,u_{xy}+\cdot607\,u_{yz}-\cdot108\,u_{zx}$$

$$1\cdot355\,\Delta\Phi_{3,8,2} = \cdot2644\,u_{xx}-\cdot241\,u_{yy}-\cdot013\,u_{zz}+\cdot2558\,u_{xy}-\cdot2297\,u_{yz}+\cdot576\,u_{zx}$$

$$1\cdot355\,\Delta\Phi_{5,11,6} = \cdot2644\,u_{xx}-\cdot241\,u_{yy}-\cdot013\,u_{zz}-\cdot2558\,u_{xy}-\cdot2297\,u_{yz}-\cdot576\,u_{zx}$$

Each silicon atom is joined to four oxygen atoms so that at each Si atom there are six $^{O}\diagdown$Si—O angles and also six O—O distances. As each Si atom is shared by two unit cells, the contribution of the six angles and the six O—O distances will be equally shared by the two unit cells. As there are six silicon atoms to a unit cell there are 36 $^{O}\diagdown$Si—O angles and 36 O—O distances to be considered. The variations of 18 of these $^{O}\diagdown$Si—O angles and O—O distances are given below and the variations of the remaining 18 are also the same. These latter are the 18 $^{O}\diagdown$Si—O angles and

the 18 O—O distances at silicon atoms 3, 4, 5 whose variations are the same as those of the $^{O}\!\diagdown$Si—O angles and O—O distances at silicon atoms 6, 1, 2 respectively.

The variations ($\Delta\phi_i$) of the various $^{O}\!\diagdown$Si—O angles are given by

$$
\begin{aligned}
2{\cdot}436\,\Delta\phi_{7,1,9_1} &= 1{\cdot}031\,u_{xx} - 2{\cdot}038\,u_{yy} + 1{\cdot}015\,u_{zz} - {\cdot}4245\,u_{xy} - 1{\cdot}012\,u_{yz} + 1{\cdot}093\,u_{zx}\\
2{\cdot}436\,\Delta\phi_{12,1,10_1} &= 1{\cdot}031\,u_{xx} - 2{\cdot}038\,u_{yy} + 1{\cdot}015\,u_{zz} + {\cdot}4245\,u_{xy} - 1{\cdot}012\,u_{yz} - 1{\cdot}093\,u_{zx}\\
2{\cdot}414\,\Delta\phi_{12,1,9_1} &= {\cdot}989\,u_{xx} + 1{\cdot}008\,u_{yy} - 1{\cdot}982\,u_{zz} + 1{\cdot}124\,u_{xy} + 1{\cdot}022\,u_{yz} + {\cdot}2516\,u_{zx}\\
2{\cdot}414\,\Delta\phi_{7,1,10_1} &= {\cdot}989\,u_{xx} + 1{\cdot}008\,u_{yy} - 1{\cdot}982\,u_{zz} - 1{\cdot}124\,u_{xy} + 1{\cdot}022\,u_{yz} - {\cdot}2516\,u_{zx}\\
2{\cdot}305\,\Delta\phi_{9_1,1,10_1} &= -2{\cdot}102\,u_{xx} + {\cdot}4841\,u_{yy} + 1{\cdot}619\,u_{zz} + {\cdot}886\,u_{yz}\\
2{\cdot}207\,\Delta\phi_{7,1,12} &= -1{\cdot}928\,u_{xx} + 1{\cdot}519\,u_{yy} + {\cdot}409\,u_{zz} - {\cdot}7868\,u_{yz}\\
2{\cdot}436\,\Delta\phi_{8,2,10_2} &= -1{\cdot}6404\,u_{xx} + {\cdot}626\,u_{yy} + 1{\cdot}015\,u_{zz} + 1{\cdot}1146\,u_{xy} + 1{\cdot}451\,u_{yz} - {\cdot}3294\,u_{zx}\\
2{\cdot}414\,\Delta\phi_{7,2,10_2} &= {\cdot}0294\,u_{xx} + 1{\cdot}96\,u_{yy} - 1{\cdot}982\,u_{zz} - {\cdot}568\,u_{xy} - {\cdot}728\,u_{yz} + {\cdot}7592\,u_{zx}\\
2{\cdot}414\,\Delta\phi_{8,2,11_2} &= 1{\cdot}974\,u_{xx} + {\cdot}0221\,u_{yy} - 1{\cdot}982\,u_{zz} + {\cdot}572\,u_{xy} - {\cdot}294\,u_{yz} + 1{\cdot}009\,u_{zx}\\
2{\cdot}436\,\Delta\phi_{7,2,11_2} &= -{\cdot}905\,u_{xx} - {\cdot}104\,u_{yy} + 1{\cdot}015\,u_{zz} + 1{\cdot}561\,u_{xy} - {\cdot}439\,u_{yz} - 1{\cdot}421\,u_{zx}\\
2{\cdot}305\,\Delta\phi_{7,2,8} &= -{\cdot}163\,u_{xx} - 1{\cdot}457\,u_{yy} + 1{\cdot}619\,u_{zz} - 1{\cdot}122\,u_{xy} - {\cdot}443\,u_{yz} + {\cdot}767\,u_{zx}\\
2{\cdot}207\,\Delta\phi_{10_2,2,11_2} &= {\cdot}658\,u_{xx} - 1{\cdot}067\,u_{yy} + {\cdot}409\,u_{zz} - 1{\cdot}467\,u_{xy} + {\cdot}395\,u_{yz} - {\cdot}683\,u_{zx}\\
2{\cdot}436\,\Delta\phi_{9_1,6,11} &= -1{\cdot}6404\,u_{xx} + {\cdot}626\,u_{yy} + 1{\cdot}015\,u_{zz} - 1{\cdot}1146\,u_{xy} + 1{\cdot}451\,u_{yz} + {\cdot}3294\,u_{zx}\\
2{\cdot}436\,\Delta\phi_{8_2,6,12} &= -{\cdot}905\,u_{xx} - {\cdot}104\,u_{yy} + 1{\cdot}015\,u_{zz} - 1{\cdot}561\,u_{xy} - {\cdot}439\,u_{yz} + 1{\cdot}421\,u_{zx}\\
2{\cdot}414\,\Delta\phi_{9_2,6,12} &= {\cdot}0294\,u_{xx} + 1{\cdot}96\,u_{yy} - 1{\cdot}982\,u_{zz} + {\cdot}568\,u_{xy} - {\cdot}728\,u_{yz} - {\cdot}7592\,u_{zx}\\
2{\cdot}414\,\Delta\phi_{8_2,6,11} &= 1{\cdot}974\,u_{xx} + {\cdot}0221\,u_{yy} - 1{\cdot}982\,u_{zz} - {\cdot}572\,u_{xy} - {\cdot}294\,u_{yz} - 1{\cdot}009\,u_{zx}\\
2{\cdot}305\,\Delta\phi_{11,6,12} &= -{\cdot}163\,u_{xx} - 1{\cdot}457\,u_{yy} + 1{\cdot}619\,u_{zz} + 1{\cdot}122\,u_{xy} - {\cdot}443\,u_{yz} - {\cdot}767\,u_{zx}\\
2{\cdot}207\,\Delta\phi_{8_2,6,9_2} &= {\cdot}658\,u_{xx} - 1{\cdot}067\,u_{yy} + {\cdot}409\,u_{zz} + 1{\cdot}467\,u_{xy} + {\cdot}395\,u_{yz} + {\cdot}683\,u_{zx}
\end{aligned}
$$

The variations (ΔR_i) of the O − O distances are given by

$$
\begin{aligned}
2{\cdot}52\,\Delta R_{7,9_1} &= 2{\cdot}788\,u_{xx} + {\cdot}3307\,u_{yy} + 3{\cdot}232\,u_{zz} - {\cdot}9603\,u_{xy} - 1{\cdot}035\,u_{yz} + 3{\cdot}002\,u_{zx}\\
2{\cdot}52\,\Delta R_{12,10_1} &= 2{\cdot}788\,u_{xx} + {\cdot}3307\,u_{yy} + 3{\cdot}232\,u_{zz} + {\cdot}9603\,u_{xy} - 1{\cdot}035\,u_{yz} - 3{\cdot}002\,u_{zx}\\
2{\cdot}52\,\Delta R_{7,11_2} &= 1{\cdot}777\,u_{xx} + 1{\cdot}341\,u_{yy} + 3{\cdot}232\,u_{zz} + 1{\cdot}544\,u_{xy} - 2{\cdot}082\,u_{yz} - 2{\cdot}397\,u_{zx}\\
2{\cdot}52\,\Delta R_{12,8_2} &= 1{\cdot}777\,u_{xx} + 1{\cdot}341\,u_{yy} + 3{\cdot}232\,u_{zz} - 1{\cdot}544\,u_{xy} - 2{\cdot}082\,u_{yz} + 2{\cdot}397\,u_{zx}\\
2{\cdot}551\,\Delta R_{12,9_1} &= 2{\cdot}788\,u_{xx} + 3{\cdot}434\,u_{yy} + {\cdot}2894\,u_{zz} + 3{\cdot}096\,u_{xy} + {\cdot}9979\,u_{yz} + {\cdot}8982\,u_{zx}\\
2{\cdot}551\,\Delta R_{7,10_1} &= 2{\cdot}788\,u_{xx} + 3{\cdot}434\,u_{yy} + {\cdot}2894\,u_{zz} - 3{\cdot}096\,u_{xy} + {\cdot}9979\,u_{yz} - {\cdot}8982\,u_{zx}\\
2{\cdot}52\,\Delta R_{8,10_2} &= {\cdot}1136\,u_{xx} + 3{\cdot}003\,u_{yy} + 3{\cdot}232\,u_{zz} + {\cdot}5826\,u_{xy} + 3{\cdot}117\,u_{yz} + {\cdot}606\,u_{zx}\\
2{\cdot}52\,\Delta R_{11,9_2} &= {\cdot}1136\,u_{xx} + 3{\cdot}003\,u_{yy} + 3{\cdot}232\,u_{zz} - {\cdot}5826\,u_{xy} + 3{\cdot}117\,u_{yz} - {\cdot}606\,u_{zx}\\
2{\cdot}551\,\Delta R_{8,11_2} &= 5{\cdot}954\,u_{xx} + {\cdot}2694\,u_{yy} + {\cdot}2894\,u_{zz} + 1{\cdot}267\,u_{xy} + {\cdot}2793\,u_{yz} + 1{\cdot}313\,u_{zx}\\
2{\cdot}551\,\Delta R_{11,8_2} &= 5{\cdot}954\,u_{xx} + {\cdot}2694\,u_{yy} + {\cdot}2894\,u_{zz} - 1{\cdot}267\,u_{xy} + {\cdot}2793\,u_{yz} - 1{\cdot}313\,u_{zx}\\
2{\cdot}551\,\Delta R_{7,10_2} &= {\cdot}592\,u_{xx} + 5{\cdot}626\,u_{yy} + {\cdot}2894\,u_{zz} - 1{\cdot}825\,u_{xy} - 1{\cdot}277\,u_{yz} + {\cdot}4139\,u_{zx}\\
2{\cdot}551\,\Delta R_{12,9_2} &= {\cdot}592\,u_{xx} + 5{\cdot}626\,u_{yy} + {\cdot}2894\,u_{zz} + 1{\cdot}825\,u_{xy} - 1{\cdot}277\,u_{yz} - {\cdot}4139\,u_{zx}\\
2{\cdot}734\,\Delta R_{7,12} &= 5{\cdot}896\,u_{yy} + 1{\cdot}588\,u_{zz} - 3{\cdot}0586\,u_{yz}\\
2{\cdot}663\,\Delta R_{9,10} &= 1{\cdot}632\,u_{yy} + 5{\cdot}456\,u_{zz} + 2{\cdot}9844\,u_{yz}\\
2{\cdot}663\,\Delta R_{7,8} &= 1{\cdot}226\,u_{xx} + {\cdot}4083\,u_{yy} + 5{\cdot}456\,u_{zz} - {\cdot}7068\,u_{xy} - 1{\cdot}493\,u_{yz} + 2{\cdot}584\,u_{zx}\\
2{\cdot}663\,\Delta R_{11,12} &= 1{\cdot}226\,u_{xx} + {\cdot}4083\,u_{yy} + 5{\cdot}456\,u_{zz} + {\cdot}7068\,u_{xy} - 1{\cdot}493\,u_{yz} - 2{\cdot}584\,u_{zx}\\
2{\cdot}734\,\Delta R_{9,8} &= 4{\cdot}423\,u_{xx} + 1{\cdot}474\,u_{yy} + 1{\cdot}588\,u_{zz} + 2{\cdot}553\,u_{xy} + 1{\cdot}53\,u_{yz} + 2{\cdot}65\,u_{zx}\\
2{\cdot}734\,\Delta R_{10,11} &= 4{\cdot}423\,u_{xx} + 1{\cdot}474\,u_{yy} + 1{\cdot}588\,u_{zz} - 2{\cdot}553\,u_{xy} + 1{\cdot}53\,u_{yz} - 2{\cdot}65\,u_{zx}
\end{aligned}
$$

3. *Calculation of the Energy due to Strain*

If K be the force-constant of Si − O valence, K_1 and K_2 the force-constants of angular deformations of Si⟨O⟩Si and O⟨Si⟩O angles respectively and K_3 the force-constant O − O repulsion, then the energy U per unit cell is given by

$$2\,U = \sum_{i=12}^{i=1} K\,(\Delta r_i)^2 + \sum_{i=6}^{i=1} K_1\,(\Delta \Phi_i)^2 + \tfrac{1}{2} \sum_{i=36}^{i=1} K_2\,(\Delta\phi_i)^2 + \tfrac{1}{2} \sum_{i=36}^{i=1} K_3\,(\Delta R_i)^2.$$

The energy of the strain per unit volume is then U/V where V is the volume of the unit cell. A unit cell of α-quartz contains three molecules of SiO_2. The volume of the unit cell obtained from the relation $V = 3m/\rho N$ where m is the molecular weight, ρ the density, N the Avagadro's number ($6{\cdot}06 \times 10^{23}$), is $111{\cdot}2 \times 10^{-24}$ c.c. The same volume is obtained from the geometry of the figure. The area included within the irregular hexagon formed by joining the silicon atoms of the unit cell is $15{\cdot}365 \times 10^{-16}$ sq. cm. Three such hexagons enclose a triangle of Si atoms of area $2{\cdot}62 \times 10^{-16}$ sq. cm. There are six such triangles, one corresponding to each side of the irregular hexagon, of total area 15·72 sq. cm. which have not been included in the hexagons. Hence in averaging over the whole space the volume of the unit cell $= (15{\cdot}365 + \frac{1}{3} \times 15{\cdot}72) \times 5{\cdot}394 \times 10^{-24}$ c.c. $= 111{\cdot}2 \times 10^{-24}$ c.c. (the length of the c-axis for α-quartz is $5{\cdot}394 \times 10^{-8}$ cm.). The energy of the strain per unit volume is therefore

$$\frac{1}{2 \times 111{\cdot}2}\left[\sum_{12} K\,(\Delta r_i)^2 + \sum_{6} K_1\,(\Delta\Phi_i)^2 + \tfrac{1}{2}\sum_{36} K_2\,(\Delta\phi_i)^2 + \tfrac{1}{2}\sum_{36} K_3\,(\Delta R_i)^2\right] \times 10^{24}.$$

On substituting the values of Δr_i, $\Delta\Phi_i$, $\Delta\phi_i$, ΔR_i the above expression becomes

$$\frac{1}{222{\cdot}4}\,[(5{\cdot}20\,K^1 + {\cdot}2415\,K_1 + 4{\cdot}997\,K_2 + 22{\cdot}5\,K_3^1)(u_{xx}^2 + u_{yy}^2) + (4{\cdot}797\,K^1 + 6{\cdot}668\,K_2 + 23{\cdot}5\,K_3^1)\,u_{zz}^2 + 2\,(1{\cdot}729\,K^1 - {\cdot}2403\,K_1 - 1{\cdot}638\,K_2 + 7{\cdot}49\,K_3^1)\,u_{zz}\,u_{yy} + 2\,(2{\cdot}87\,K^1 - 3{\cdot}344\,K_2 + 9{\cdot}35\,K_3^1)\,u_{xx}\,(u_{xx} + u_{yy}) + (1{\cdot}729\,K^1 + {\cdot}241\,K_1 + 3{\cdot}314\,K_2 + 7{\cdot}5\,K_3^1)\,u_{xy}^2 + (2{\cdot}87\,K^1 + {\cdot}627\,K_1 + 2{\cdot}094\,K_2 + 9{\cdot}35\,K_3^1)(u_{yz}^2 + u_{zx}^2) + 2\,({\cdot}6026\,K^1 + {\cdot}181\,K_1 - {\cdot}781\,K_2 + {\cdot}465\,K_3^1)(u_{xx}u_{yz} - u_{yy}u_{yz} + u_{zz}u_{xy})] \times 10^{24}$$ where $K^1 = K \times 10^{-16}$, $K_3^1 = K_3 \times 10^{-16}$.

4. *Expressions for Elastic Constants*

α-Quartz belongs to the point-group D_3, and according to the figure it has an axis of twofold symmetry in the x-axis. The energy of the strian

per unit volume in terms of the elastic constants for a crystal belonging to this point-group is given by (Love, *vide* ref. 5).

$$\tfrac{1}{2}[c_{11}(u_{xx}^2+u_{yy}^2)+c_{33}u_{zz}^2+2c_{12}u_{xx}u_{yy}+2c_{13}u_{zz}(u_{xx}+u_{yy})+c_{66}u_{xy}^2+c_{44}(u_{zz}^2+u_{yz}^2)$$
$$+2c_{14}(u_{zz}u_{yz}-u_{yy}u_{yz}+u_{zz}u_{xy})]$$

The expression given by Love relates to the axis of symmetry being the y-axis. It becomes identical with our expression if we put $x = -y$ and $y = x$ in it thereby changing e_{xy}, e_{xz}, e_{yz} in the expression given by Love into $-u_{xy}$, $-u_{yz}$, $-u_{xz}$ respectively of our expression. c_{11}, c_{12}, c_{13}, c_{14}, c_{66}, c_{33}, c_{44} are the seven elastic constants of α-quartz. They can now be expressed in terms of the force-constants K, K_1, K_2, K_3. We have

$$c_{11} = \frac{1}{111\cdot2}[5\cdot2\ \ K\times10^{-16}+\cdot2415\ K_1+4\cdot997\ K_2+22\cdot5\ \ K_3\times10^{-16}]\times10^{24}$$

$$c_{12} = \frac{1}{111\cdot2}[1\cdot729\ \ K\times10^{-16}-\cdot2403\ K_1-1\cdot638\ K_2+\ 7\cdot49\ \ K_3\times10^{-16}]\times10^{24}$$

$$c_{33} = \frac{1}{111\cdot2}[4\cdot797\ \ K\times10^{-16}\qquad\qquad +6\cdot668\ K_2+23\cdot5\ \ K_3\times10^{-16}]\times10^{24}$$

$$c_{13} = \frac{1}{111\cdot2}[2\cdot87\ \ K\times10^{-16}\qquad\qquad -3\cdot344\ K_2+\ 9\cdot35\ \ K_3\times10^{-16}]\times10^{24}$$

$$c_{44} = \frac{1}{111\cdot2}[2\cdot87\ \ K\times10^{-16}+\cdot627\ K_1+2\cdot094\ K_2+\ 9\cdot35\ \ K_3\times10^{-16}]\times10^{24}$$

$$c_{14} = \frac{1}{111\cdot2}[\ \cdot6026\ K\times10^{-16}+\cdot181\ K_1-\ \cdot781\ K_2+\ \ \cdot465\ K_3\times10^{-16}]\times10^{24}$$

$$c_{66} = \frac{1}{111\cdot2}[1\cdot729\ \ K\times10^{-16}+\cdot241\ K_1+3\cdot314\ K_2+\ 7\cdot5\ \ K_3\times10^{-16}]\times10^{24}$$

We find from these relations that $c_{11} - c_{12} = 2c_{66}$.

5. *Expressions for Force-Constants from Raman Effect Data*

In an earlier paper the author had calculated the three force-constants of Si—O valence (K), of $^{Si}\!\diagdown$O—Si and $^{O}\!\diagdown$Si—O deformation (K_1, K_2) from the Raman effect data. For the calculation of the elastic constants we have used a fourth constant K_3 that of O—O repulsion. It is therefore necessary to calculate the four constants again. In order to calculate the force-constants we use the four frequencies in the Raman spectrum of α-quartz which belong to the totally symmetric class. They are 207, 356, 466, 1082 cm.$^{-1}$ The potential energy and the kinetic energy of the vibration can be written down by the use of symmetry co-ordinates and the frequencies calculated.

If Δr, ΔR represent the variations of Si—O and O—O distances, and $\Delta\Phi$ and $\Delta\phi$ the variations of $^{Si}\!\diagdown$O—Si and $^{O}\!\diagdown$Si—O angles respectively and if K, K_1, K_2, K_3 represent the force-constants of Si — O valence,

$\overset{Si}{\diagdown}O-Si$ and $\overset{O}{\diagdown}Si-O$ deformation, and O−O repulsion respectively the potential energy of each unit cell is given by

$$2V = K \sum_{12} (\Delta r)^2 + K_1 \sum_{6}' (\Delta\Phi)^2 + \tfrac{1}{2} K_2 \sum_{36} (\Delta\phi)^2 + \tfrac{1}{2} K_3 \sum_{36} (\Delta R)^2.$$

There are twelve Si−O bonds and six $\overset{Si}{\diagdown}O-Si$ angles in each unit cell. Further four oxygen atoms are bound to each silicon atom and so we have to consider six $\overset{O}{\diagdown}Si-O$ angles and six O−O distances at each silicon atom or thirty-six $\overset{O}{\diagdown}Si-O$ angles and thirty-six O−O distances for the whole cell. As each silicon atom is common to two cells, the contributions to the potential energy due to these $\overset{O}{\diagdown}Si-O$ angles and O−O distances will be equally shared by the two cells. For finding the variations of $\overset{O}{\diagdown}Si-O$ angles we have to consider the oxygen atoms like 9_1, 10_1 in the adjacent cells.

The symmetry co-ordinates corresponding to the four totally symmetric frequencies are

(i) $x_7+x_8+x_9+x_{10}+x_{11}+x_{12}$
(ii) $x_2+x_4+x_6-x_1-x_3-x_5$
(iii) $y_7+y_9+y_{11}-y_8-y_{10}-y_{12}$
(iv) $z_8+z_{10}+z_{12}-z_7-z_9-z_{11}$,

where x_i, y_i, z_i represent the motion of ith atom with respect to its position of rest as origin. Each x_i is directed towards a point in the basal plane containing the given atom where the threefold axis meets it, z_i is perpendicular to the basal plane and positive upwards and y_i is at right angles to both and positive in a direction making the motion right-handed. Let β, γ, δ, ϵ be the displacement of atoms in the four modes. The variations of Si − O distances are given by

$$\Delta r_{2,8} = \Delta r_{2,7} = \Delta r_{6,12} = \Delta r_{6,11} = \Delta r_{4,10} = \Delta r_{4,9}$$
$$= \frac{\cdot 5974\,\beta - \cdot 8644\,\gamma + \cdot 8946\,\delta - 1\cdot 168\,\epsilon}{1\cdot 588} = \Delta p_1$$
$$\Delta r_{7,1} = \Delta r_{1,12} = \Delta r_{5,11} = \Delta r_{5,10} = \Delta r_{3,9} = \Delta r_{3,8}$$
$$= \frac{-\cdot 1676\,\beta + \cdot 8054\,\gamma - 1\cdot 147\,\delta + \cdot 63\,\epsilon}{1\cdot 588} = \Delta p_2$$

The variations of $\overset{Si}{\diagdown}O-Si$ angles are given by

$$\Delta\Phi_{2,7,1} = \Delta\Phi_{1,12,6} = \Delta\Phi_{5,11,6} = \Delta\Phi_{5,10,4} = \Delta\Phi_{4,9,3} = \Delta\Phi_{3,8,2}$$
$$= \frac{-\cdot 7914\,\beta - \cdot 4783\,\gamma + 1\cdot 018\,\delta + \cdot 9915\,\epsilon}{1\cdot 355} = \Delta\Phi$$

The variations of $^{O}\!\diagdown$Si—O angles at silicon atom (1) are

$$\Delta\phi_{7,1,12} = \frac{-2{\cdot}634\,\beta - 2{\cdot}391\,\gamma + {\cdot}585\,\delta + {\cdot}651\,\epsilon}{2{\cdot}207} = \Delta\phi_1$$

$$\Delta\phi_{9,1,10_1} = \frac{-2{\cdot}546\,\beta + 2{\cdot}431\,\gamma - {\cdot}1138\,\delta - 1{\cdot}387\,\epsilon}{2{\cdot}305} = \Delta\phi_2$$

$$\Delta\phi_{9\,1\,7} = \Delta\phi_{12,1,10_1} = \frac{2{\cdot}131\,\beta + {\cdot}0743\,\gamma - {\cdot}796\,\delta + {\cdot}6774\,\epsilon}{2{\cdot}436} = \Delta\phi_3$$

$$\Delta\phi_{7,1,10_1} = \Delta\phi_{12,1,10_2} = \frac{{\cdot}4688\,\beta + {\cdot}07607\,\gamma + {\cdot}5286\,\delta - {\cdot}3824\,\epsilon}{2{\cdot}414}$$

The variations of O — O distances at silicon atom (1) are

$$\Delta R_{7,12} = \frac{-3{\cdot}132\,\beta - 3{\cdot}712\,\delta + 2{\cdot}52\,\epsilon}{2{\cdot}734} = \Delta R_1$$

$$\Delta R_{9_1,10_1} = \frac{-{\cdot}8676\,\beta + 2{\cdot}405\,\delta - 4{\cdot}672\,\epsilon}{2{\cdot}662} = \Delta R_2$$

$$\Delta R_{9_1,7} = \Delta R_{12,10_1} = \frac{2{\cdot}672\,\beta - 1{\cdot}491\,\delta}{2{\cdot}52} = \Delta R_3$$

$$\Delta R_{7,10_1} = \Delta R_{12,9_1} = \frac{1{\cdot}023\,\beta - {\cdot}1834\,\delta - 1{\cdot}076\,\epsilon}{2{\cdot}551} = \Delta R_4$$

The variations of O—O distances and $^{O}\!\diagdown$Si—O angles at all other silicon atoms are the same as these. Hence the potential energy becomes

$$2V = 6K\{(\Delta p_1)^2 + (\Delta p_2)^2\} + 6K_1(\Delta\Phi)^2 + \tfrac{1}{2}6K_2\{(\Delta\phi_1)^2 + (\Delta\phi_2)^2 + 2(\Delta\phi_3)^2 + 2(\Delta\phi_4)^2\} + \tfrac{1}{2}6K_3\{(\Delta R_1)^2 + (\Delta R_2)^2 + 2(\Delta R_3)^2 + 2(\Delta R_4)^2\}$$

On expanding it becomes

$$2V = 6[a\beta^2 + b\gamma^2 + c\delta^2 + d\epsilon^2 - 2e\beta\gamma + 2f\beta\delta - 2g\beta\epsilon - 2h\gamma\delta + 2i\gamma\epsilon - 2j\delta\epsilon]$$

where

$$\begin{aligned}
a &= {\cdot}1525\,K + {\cdot}3412\,K_1 + 2{\cdot}124\,K_2 + 1{\cdot}993\,K_3\\
b &= {\cdot}5535\,K + {\cdot}1264\,K_1 + 1{\cdot}144\,K_2\\
c &= 1{\cdot}1476\,K + {\cdot}5641\,K_1 + {\cdot}1911\,K_2 + 1{\cdot}685\,K_3\\
d &= {\cdot}6984\,K + {\cdot}5356\,K_1 + {\cdot}3271\,K_2 + 2{\cdot}141\,K_3\\
e &= {\cdot}2581\,K - {\cdot}2061\,K_1 - {\cdot}0973\,K_2\\
f &= {\cdot}3080\,K - {\cdot}4388\,K_1 - {\cdot}3744\,K_2 - {\cdot}027\,K_3\\
g &= {\cdot}3184\,K + {\cdot}4274\,K_1 - {\cdot}3688\,K_2 + {\cdot}4091\,K_3\\
h &= {\cdot}7687\,K + {\cdot}2652\,K_1 + {\cdot}1725\,K_2\\
i &= {\cdot}6015\,K - {\cdot}2583\,K_1 - {\cdot}4734\,K_2\\
j &= {\cdot}7757\,K - {\cdot}5495\,K_1 + {\cdot}071\,K_2 + 1{\cdot}386\,K_3
\end{aligned}$$

Since each silicon atom is linked to two cells, the kinetic energy due to these will be equally shared by the two cells. The kinetic energy is given by $2T = 6m_1\dot{\beta}^2 + 3m_2\dot{\gamma}^2 + 6m_1\dot{\delta}^2 + 6m_1\dot{\epsilon}^2$ where $m_1 = 16$ and $m_2 = 28{\cdot}3$.

The frequencies in cm.$^{-1}$ are given by the determinant

$$\begin{vmatrix} (a-16\lambda^2) & -e & f & -g \\ -e & (b-14{\cdot}15\lambda^2) & -h & i \\ f & -h & (c-16\lambda^2) & -j \\ -g & i & -j & (d-16\lambda^2) \end{vmatrix} = 0 \qquad (5{\cdot}1)$$

where the frequency ω (in cm.$^{-1}$) $= \dfrac{\lambda}{2\pi c} \times \sqrt{\dfrac{10^{21}}{1{\cdot}65}} = 1307\lambda$

6. *Calculation of Force-Constants, Raman Frequencies and Elastic Constants*

On expanding the determinant we get

$$\begin{aligned} &57958{\cdot}4\,\lambda^8 - [9506\,K + 5730{\cdot}4\,K_1 + 14255{\cdot}6\,K_2 + 21078{\cdot}7\,K_3]\,\lambda^6 \\ &+ [86{\cdot}83\,K^2 + 905{\cdot}8\,K_2^2 + 2069{\cdot}8\,K_3^2 + 871{\cdot}6KK_1 + 2151{\cdot}5\,KK_2 + 2070{\cdot}1\,KK_3 \\ &+ 1058{\cdot}7\,K_1K_2 + 1715{\cdot}6\,K_1K_3 + 4014\,K_2K_3]\,\lambda^4 - [7{\cdot}04\,K_2^3 + 43{\cdot}1\,K_3^3 \\ &+ 115{\cdot}5\,KK_2^2 + 126{\cdot}8\,KK_3^2 + {\cdot}848\,K^2K_1 + 16{\cdot}46\,K^2K_2 + 12{\cdot}54\,K^2K_3 + 240{\cdot}0\,K_2K_3^2 \\ &+ 190{\cdot}9\,K_2^2K_3 + 44{\cdot}89\,K_1K_2^2 + 111{\cdot}7\,K_1K_3^2 + {\cdot}63\,K_1^2K_3 + 148{\cdot}4\,KK_1K_2 \\ &+ 124{\cdot}6\,KK_1K_3 + 253{\cdot}4\,KK_2K_3 + 238{\cdot}8\,K_1K_2K_3]\,\lambda^2 + [{\cdot}1063\,KK_2^3 \\ &+ {\cdot}7430\,K^2K_2^2 + {\cdot}4121\,K^2K_3^2 + 5{\cdot}433\,KK_2K_3^2 + 4{\cdot}243\,KK_2^2K_3 \\ &+ 5{\cdot}032\,KK_1K_2^2 + 3{\cdot}193\,KK_1K_3^2 + {\cdot}0467\,KK_1^2K_3 + {\cdot}0959\,K^2K_1K_2 \\ &+ {\cdot}0798\,K^2K_1K_3 + 1{\cdot}111\,K^2K_2K_3 + 8{\cdot}035\,KK_1K_2K_3 + {\cdot}3150\,K_2^3K_1 \\ &+ 6{\cdot}264\,K_1K_2K_3^2 + 7{\cdot}431\,K_1K_2^2K_3 + {\cdot}0052\,K_1^2K_2^2 + {\cdot}0356\,K_1^2K_2K_3 \\ &+ 4{\cdot}624\,K_2^2K_3^2 + {\cdot}2759\,K_2^3K_3 + 1{\cdot}687\,KK_3^3 + 3{\cdot}794\,K_3^3K_2 + {\cdot}3796\,K_1K_3^3] = 0 \qquad (6{\cdot}1) \end{aligned}$$

If the observed frequencies are the roots of the given equation, it should be given by

$$\lambda^8 - {\cdot}9122\,\lambda^6 + {\cdot}1698\,\lambda^4 - {\cdot}01017\,\lambda^2 + {\cdot}0001625 = 0 \qquad (6{\cdot}2)$$

These two equations (6·1) and (6·2) give four expressions for the determination of the four force-constants K, K_1, K_2, K_3, but it is extremely difficult to determine the constants in this way. It was therefore thought that if the same force-constants hold for the elastic constants as well as the Raman frequencies, the expressions for the elastic constants may be utilised to determine these constants. These expressions are much more convenient to work with as the force-constants occur with power-index one in them. The expressions for c_{13} and c_{33} were chosen for this purpose, and two equations obtained from the expanded determinant were used. If K and K_3 are expressed in terms of 10^5 dynes and K_1 and K_2 in terms of 10^{-11} dynes/radian, and using $c_{33} = 10{\cdot}5 \times 10^{11}$ dynes, $c_{13} = 1{\cdot}41 \times 10^{11}$ dynes we get from the expressions of elastic constants for c_{33} and c_{13}

$$4{\cdot}797\,K + 6{\cdot}668\,K_2 + 23{\cdot}5\,K_3 = 11{\cdot}68 \qquad (6{\cdot}3)$$

$$2{\cdot}87\,K - 3{\cdot}344\,K_2 + 9{\cdot}35\,K_3 = 1{\cdot}58 \qquad (6{\cdot}4)$$

The expanded determinant (6·1) gives the two relations

$$\cdot 1640\,K + \cdot 09887\,K_1 + \cdot 246\,K_2 + \cdot 3475\,K_3 = \cdot 9122 \qquad (6\cdot 5)$$

and $[\cdot 001498\,K^2 + \cdot 01567\,K_2^2 + \cdot 03571\,K_3^2 + \cdot 01504\,KK_1 + \cdot 03712\,KK_2 + \cdot 03572\,KK_3$

$$+ \cdot 01827\,K_1K_2 + \cdot 0296\,K_1K_3 + \cdot 06926\,K_2K_3) = \cdot 1698 \qquad (6\cdot 6)$$

From equations (6·3), (6·4), (6·5) we get

$$K_1 = 6\cdot 621 - 1\cdot 111\,K\ ;\ K_2 = \cdot 5121 + \cdot 1603\,K\ ;\ K_3 = \cdot 3518 - \cdot 2498\,K.$$

On substituting these values in (6·6) and solving the quadratic for K we get $K = 5\cdot 01 \times 10^5$ dynes which gives

$$K_1 = 1\cdot 056 \times 10^{-11}\ \text{dynes/radian}\ ;\ K_2 = 1\cdot 315 \times 10^{-11},\ K_3 = -\cdot 8992 \times 10^5\ \text{dynes}.$$

Substituting these values in the original determinant (5·1) we get the equation

$$57958\cdot 4\,\lambda^8 - 53463\cdot 6\,\lambda^6 + 9970\cdot 5\,\lambda^4 - 536\cdot 3\,\lambda^2 + 7\cdot 55 = 0 \qquad (6\cdot 7)$$

which gives the following values of frequencies in cm.$^{-1}$

$\bar{\omega}$ (calc.)	1087,	508,	310,	195
$\bar{\omega}$ (obs.)	1082,	466,	366,	207

Using another set of force-constants (by slightly altering K_1 and K_2) namely $K = 4\cdot 98 \times 10^5$, $K_1 = \cdot 454 \times 10^{-11}$, $K_2 = 1\cdot 565 \times 10^{-11}$, $K_3 = -\cdot 892$ we get from (5·1) the equation

$$57958\cdot 4\,\lambda^8 - 53448\cdot 2\,\lambda^6 + 10012\cdot 2\,\lambda^4 - 570\cdot 4\,\lambda^2 + 8\cdot 426 = 0 \qquad (6\cdot 8)$$

which gives the frequencies 1087, 491, 333, 198.

Table II gives the force-constants, Raman frequencies and the calculated values of elastic constants. The observed values of the latter are due to Voigt.[6]

TABLE II

Force-constants				Calculated values of Raman frequencies				Calculated values of elastic constants							
$K\times 10^{-5}$	$K_1\times 10^{11}$	$K_2\times 10^{11}$	$K_3\times 10^{-5}$					$C_{11}\times 10^{-11}$	$C_{12}\times 10^{-11}$	$C_{13}\times 10^{-11}$	$C_{33}\times 10^{-11}$	$C_{44}\times 10^{-11}$	$C_{14}\times 10^{-11}$	$C_{66}\times 10^{-11}$	$\gamma\times 10^{-11}$
4·98	·454	1·565	−·892	1087	491	333	198	12·3	−·64	·65	12·0	8·5	1·30	6·4	4·47
5·01	1·056	1·315	−·8992	1087	508	310	195	11·3	−·44	1·40	10·5	8·4	1·59	5·87	4·38
	Observed values		→	1082	466	356	207	8·68	·73	1·41	10·5	5·82	1·73	3·98	3·85

The compressibility η has been calculated from the relation $\eta = \frac{(c_{11} + c_{12})\, c_{33} - 2\, c_{13}^2}{c_{11} + c_{12} + 2c_{33} - 4c_{13}}$. This expression can be readily obtained from the fundamental relations

$$-K_{xx} = c_{11}u_{xx} + c_{12}u_{yy} + c_{13}u_{zz} + c_{14}u_{yz}$$

$$-K_{yy} = c_{12}u_{xx} + x_{11}u_{yy} + c_{13}u_{zz} - c_{14}u_{yz}$$

$$-K_{zz} = c_{13}u_{xx} + c_{13}u_{yy} + c_{33}u_{zz}$$

when $K_{xx} = K_{yy} = K_{zz}$.

7. *Discussion of Results*

In the earlier paper the author had calculated the following values of force-constants

$$K = 5{\cdot}065 \times 10^5,\ K_1 = {\cdot}5116 \times 10^{-11},\ K_2 = {\cdot}9491 \times 10^{-11} \text{ dynes.}$$

We find from this investigation that value of K the force-constant of Si – O valence is very nearly the same although K_1 and K_2 are altered. An important result of the investigation is that K_3 is negative and equal to about ·89. With only three force-constants K, K_1, K_2 the elastic constants show very considerable deviations from observed values, and it is only by using K_3 that we get any approximation to the observed values.

The calculated and the observed values of elastic constants are in fair agreement for both the schemes of force-constants given in Table II, although in the second case there is slightly better agreement. A closer agreement between the observed and calculated values can hardly be expected unless all the force-constants and interaction terms are known. The investigation shows that the same scheme of force-constants holds for the elastic constants as well as for the infra-red frequencies.

8. *Summary*

The high frequencies of vibration in α-quartz and the structure of the crystal show that the silicon-oxygen bonds are largely covalent in nature. We therefore assume that in a homogeneous strain the distance from the basis to basis is altered as if the basis were rigid and attached at one point in the continuum subjected to strain. It then becomes possible to find the change in the bond distances and bond angles on the basis of the known crystal structure. Assuming the four force-constants of Si–O valence, O–O repulsion and $^{Si}\!\diagdown\!O\!-\!Si$ and $^{O}\!\diagdown\!Si\!-\!O$ deformations the potential energy per unit volume can be calculated, and comparing this with the strain energy of the crystal, the elastic constants can be calculated in terms of the force-constants.

The four force-constants have been calculated from the Raman effect data. Taking the four frequencies 207, 356, 466, 1082 belonging to the totally symmetric class, the variations of the bond distances and bond angles have been worked out by the use of symmetry co-ordinates. Using the four force-constants, the potential as well as kinetic energy of the unit cell has been obtained and the force-constants calculated by obtaining the best agreement between the calculated and observed values of Raman frequencies. The elastic constants are then calculated. The observed and calculated values of elastic constants show good agreement to a first approximation. The investigation shows that the same force-constants hold for the elastic constants and the infra-red frequencies.

In conclusion, the author thanks Sir C. V. Raman, Kt., F.R.S., N.L., for his kind interest in the work and for several valuable suggestions.

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Note added in proof.—If from Section 4 we substitute the expressions for c_{11}, c_{12}, etc., in the expression for the compressibility η given at the end of Section 6 we find that $\eta = [3{\cdot}33\,K + 13{\cdot}4\,K_3] \times \frac{10^8}{111{\cdot}2}$. The expression for compressibility thus comes out independent of the force-constants (K_1 and K_2) of angular deformation. This is to be expected since in a uniform dilatation or compression the angles do not alter and so the force-constants of angular deformation should not enter in the calculation of compressibility.

CHEMISTRY OF GOSSYPOL

Part IV. Behaviour of Gossypol as an Ortho-Hydroxy Aldehyde: Formation of α-Pyrones and Flavylium Salts

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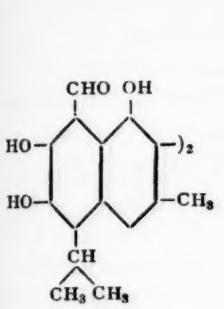
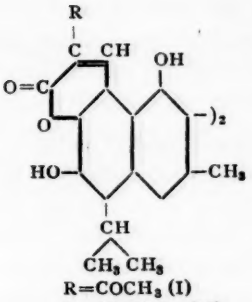
It has been established that gossypol contains six hydroxyl and two aldehyde groups in its molecule through the preparation of the hexa-acetate, the hexa-methyl ether and the dianil. But there has been no direct and conclusive evidence about the positions which these groups occupy with reference to one another. Adams and co-workers[1] observed that gossypol gave a deep red colour with pyroboroacetate and a purple red colour with stannic chloride and inferred that ortho-hydroxycarbonyl groups existed. They have used the idea to explain the properties and certain of the unusual reactions of gossypol and its derivatives. The formation of apogossypol[2] by the loss of aldehyde groups when alkali acts upon gossypol may also be adduced in favour of it. But so far the existence of this structural feature has not been definitely proved by the formation of appropriate derivatives. The work described in this memoir has been done with a view to supply this proof.

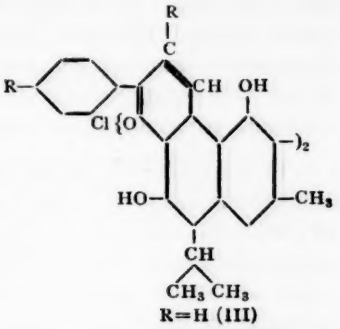
Two reactions are very characteristic of ortho-hydroxy aldehydes; one of these leads to the formation of α-pyrones by condensation with ethyl-acetoacetate and with diethylmalonate and the other to the formation of flavylium salts by condensation with acetophenone and with its derivatives in the presence of suitable condensing agents. Gossypol condenses with the above-mentioned esters with the aid of piperidine to form 3-acetyl and 3-carbethoxy-α-pyrones (I and II). These are definite crystalline compounds showing sharp difference in colour between alkaline and acid solutions. Their structures are based on Adams' formula of gossypol. They are sparingly soluble in ordinary solvents and possess high melting points. The condensation of gossypol with acetophenone and ω: 4-dihydroxy aceto-phenone takes place readily in ether or ethylacetate solution when saturated with dry hydrogen chloride. The characteristic deeply-coloured flavylium salts (III and IV) are formed and their reactions are described in the experimental part.



Gossypol



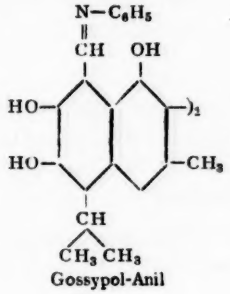
R=$COCH_3$ (I)
R=$COOC_2H_5$ (II)



R=H (III)
R=OH (IV)

Having established as given above the existence of orthohydroxy aldehyde groups in gossypol it becomes necessary to explain the total absence of difficulty in completely methylating it to hexamethyl gossypol. It has been reported already[3] that even diazomethane methylates all the hydroxyl groups of gossypol readily whereas in other cases of ortho-hydroxy carbonyl compounds difficulty has been experienced. An explanation may probably be found in the weakness of the chelation involving the hydroxyl and aldehyde groups in gossypol. That the presence of substituents in neighbouring positions can weaken chelation has been indicated by the work of Chaplin and Hunter[4] and Saunders *et al.*[4a] in other cases. Such substituents are present in the gossypol molecule.

It is interesting to record here that the above-mentioned α-pyrones and flavylium salts can also be obtained pure when gossypol-dianil is used in the place of gossypol for the condensations. The anil seems to undergo decomposition even under the mild conditions of these reactions, liberating gossypol for condensation with the ketonic esters or the ketones. In some of our previous publications[5] it has been recorded that the anil is easily decomposed by short treatment with hot acetic anhydride to yield gossypol-acetic acid



Gossypol-Anil

$+CH_3-CO-CH_2-CO_2Et \rightarrow$ I

A3*a*

and that under the ordinary conditions of methylation and acetylation it yields gossypol derivatives and not substitution products of the anil. The experiments recorded here show that even under milder conditions, *e.g.*, mixing with ethyl acetoacetate and piperidine in the cold, the decomposition liberating gossypol takes place.

In the course of the above-mentioned experiments we had occasion to examine the action of aniline on gossypol carefully. It has not been possible to obtain the tetra-anilino compound pure. Though excess of aniline is held rather tenaciously and gives the impression that a tetra-anil is formed (high values for N), the excess of aniline can be removed by careful grinding and boiling of the substance with ether or chloroform (benzene is not quite suitable for the purpose) and only the dianil is left behind. Consequently this alone should be taken as a definite anilino derivative.

Experimental

Condensation of gossypol with acetoacetic ester (I).—A mixture of gossypol (0·5 g.) and acetoacetic ester (2 c.c.) was dissolved in the requisite quantity of absolute ethyl alcohol (10 c.c.) to get a clear solution. A few drops of piperidine were added and the contents allowed to stand overnight after shaking for some time. An orange coloured precipitate slowly separated out; it was filtered and washed successively with alcohol and water.

The substance was insoluble in alcohol and other common organic solvents. It crystallised from hot pyridine as yellow thin rectangular plates, which did not melt below 330°. It dissolved in concentrated sulphuric acid giving a bright pink colour which was quite characteristic and stable. It was easily soluble in aqueous sodium hydroxide, forming again a bright pink solution which changed gradually to brown. The pink colour of a freshly made alkaline solution is changed to yellow by acid; the transition from pink to yellow and the reverse is very sharp and is a definite indication of the change from alkali to acid and *vice versa*. In this respect it compares favourably with ordinary indicators used in acidimetry-alkalimetry. The only difficulty in using this substance as an indicator is its insolubility in alcohol.

[Found in air-dried sample: C, 68·4; H, 5·4; loss on drying *in vacuo* at 120°, 2·6%; $C_{38}H_{34}O_{10}$, H_2O requires C, 68·3, H, 5·4; H_2O (loss) 2·7%. Found in the vacuum dried sample: C, 69·9; H, 5·3; $C_{38}H_{34}O_{10}$ requires C, 70·2; H, 5·2%.] Yield of the pure compound 0·3 g.

The same product was obtained even when concentrated sulphuric acid was used instead of alcohol and piperidine.

Condensation of gossypol-anil with acetoacetic ester (*I*).—Gossypol anil (0·5 g.) was dissolved in warm pyridine (15 c.c.), acetoacetic ester (2 c.c.) and a few drops of piperidine were added and the clear solution thus obtained was left over at room temperature for two days. There was only a very small quantity of precipitate which was removed by filtration. The clear filtrate on dilution with methyl alcohol (50 c.c.) gave an orange-yellow solid (0·2 g.). It did not melt below 330° and it was identical with the condensation product of acetoacetic ester and pure gossypol itself in all its properties.

This compound could be prepared in a much shorter time by heating the components in the given proportions on a boiling water-bath for two hours and working up the product as above.

[Found: C, 68·5; H, 5·6; $C_{38}H_{34}O_{10}$, H_2O requires: C, 68·3; H, 5·4%.]

Condensation of gossypol with diethyl malonate (*II*).—A mixture of gossypol (0·5 g.) and malonic ester (2 c.c.) was dissolved in the requisite quantity of absolute ethyl alcohol to get a clear solution, a few drops of piperidine were added and the contents were allowed to stand for two days. No solid had precipitated at the end of this period. The solution was then poured into about 100 c.c. of water. The precipitate thus produced was filtered and recrystallised from acetic acid and methyl alcohol, when it was obtained as yellow tiny rectangular plates, melting at 248–50°; yield (0·2 g.). With concentrated sulphuric acid it gave a red solution and its solution in sodium hydroxide had a deep red colour which changed to yellow on acidifying; the transition was quite sharp. The number of carbethoxy groups in the molecule was found by estimating the ethoxyl content by the micro-zeisel method.

[Found in the air-dried sample: C, 66·1; H, 5·6; OC_2H_5, 12·4 and loss on drying *in vacuo* at 120°, 2·6%. $C_{34}H_{28}O_8(COOC_2H_5)_2$, H_2O requires C, 66·0; H, 5·5, OC_2H_5, 12·4; H_2O (loss) 2·5%. Found in the vacuum dried sample: C, 67·5; H, 5·4; $C_{34}H_{28}O_8(COOC_2H_5)_2$ requires C, 67·6; H, 5·3%.]

Condensation of gossypol-anil with diethyl malonate (*II*).—Gossypol-anil (0·5 g.) was dissolved in warm pyridine (15 c.c.), diethyl malonate (2 c.c.) and a few drops of piperidine were added and the solution was heated on a water-bath for about two hours. The solution was filtered to remove any suspended impurities. A small quantity of the filtrate was diluted with methyl alcohol, but no precipitate was obtained. So the remaining solution was poured into water (100 c.c.) and the precipitate thus obtained (0·2 g.) was filtered and recrystallised from acetic acid. In all respects this

product was found to be identical with the condensation product obtained straight from pure gossypol itself.

[Found: C, 66·4; H, 5·5; $C_{34}H_{28}O_8$ $(COOC_2H_5)_2$, H_2O requires: C, 66·0; H, 5·5%.]

Condensation of gossypol with acetophenone (*III*).—A solution of gossypol (0·5 g.) in sodium-dried ether (20 c.c.) was prepared, pure dry acetophenone (2 c.c.) was added and the container was cooled in ice. Dry hydrogen chloride gas was passed into the solution till it was saturated (one and half hours). The initial yellow solution slowly became intense pink. The flask was stoppered well and left in the ice-chest overnight. Only a small quantity of a crystalline solid was deposited on the sides of the container; however, on adding a large amount of ether, a considerable quantity of the pyrylium salt was obtained. It was filtered and recrystallised from methyl alcohol-hydrochloric acid mixture. It was thus obtained as pink-coloured thin rectangular plates and flat needles, melting at 295–97°. Like the salts of anthocyanidins, this flavylium salt was soluble in acidulated hydroxylic solvents like alcohol to give a deep reddish-violet colour. It was insoluble in non-hydroxylic solvents like benzene, ether, etc.

[Found in air-dried sample: C, 67·7; H, 5·9; Cl, 9·0; $C_{46}H_{40}O_6Cl_2$, $3H_2O$ requires C, 67·9; H, 5·7, and Cl, 8·7%.]

Decomposition of gossypol-anil with hydrogen chloride.—To a suspension of gossypol-anil (0·5 g.) in dry ether (20 c.c.), a current of dry hydrogen chloride gas was passed. As the ether absorbed the acid fumes, the original pale yellow solution turned first to orange and finally deep brown and all the suspension went into solution. The ether solution was shaken up with water to remove aniline hydrochloride formed in the reaction and then evaporated to dryness. The brown solid thus obtained was recrystallised from methyl alcohol. A pure sample of this product melted at 184–85° and was found to be identical with gossypol.

Condensation of gossypol-anil with acetophenone (*III*).—To a suspension of gossypol-anil (0·8 g.) in sodium-dried ether (20 c.c.), dry acetophenone (2 c.c.) was added and the container cooled in ice. A current of dry hydrogen chloride gas was passed till saturation (one and half hours). The initial pale yellow solution changed first to orange and finally to deep pink as the gossypol-anil went into solution and the condensation took place. The container was stoppered well and left in the ice-chest overnight. More ether was added to it the next day and the precipitate (0·25 g.) thus obtained was filtered and recrystallised from methyl alcohol-hydrochloric acid mixture. As regards melting point, crystal structure, colour reactions and other

properties, the pyrilium salt obtained by this method was quite identical with the one prepared starting with pure gossypol itself.

[Found: C, 67·9; H, 6·0; $C_{46}H_{40}O_8Cl_2$, $3H_2O$ requires: C, 67·9; H, 5·7%.]

Condensation of gossypol with ω*: 4-dihydroxy acetophenone (IV).*— Gossypol (30 mg.) and ω: 4-dihydroxy acetophenone (20 mg.) were dissolved in sodium-dried ether (20 c.c.), the ice-cooled solution was saturated with dry hydrogen chloride gas and the contents left in the ice-chest overnight. Since the quantities of the starting materials were small, ether and hydrogen chloride were evaporated at the laboratory temperature and the residue taken up in 1% methyl alcoholic hydrogen chlroide. The pyrylium salt was precipitated from this solvent by adding concentrated hydrochloric acid. The solid thus obtained was filtered and recrystallised from the same solvent, when it was obtained as tiny rectangular plates, having a deep pink colour. It did not melt below 320°.

[Found: C, 65·1; H, 5·6; $C_{46}H_{40}O_8Cl_2$, $3H_2O$ requires: C, 65·3; H, 5·4%.]

The above-mentioned two flavylium salts gave the following colour reactions with the reagents listed below. Solutions of the salts in methyl alcohol containing 1% hydrochloric acid were used for the purpose.

Reagents	Flavylium salt obtained from gossypol and	
	(i) Acetophenone (III)	(ii) ω : 4-Dihydroxy acetophenone (IV)
1. Original colour of solution ..	Deep red-violet	Deep red ; in thin layers pink
2. Dilution with concentrated HCl	No change	No change
3. Sodium acetate solution ..	Blue	Only a small change to reddish-pink ; no change further
4. Sodium bicarbonate ..	Blue with a slight green tinge	Bluish-pink ; changes to violet-blue and fades slowly to violet-brown
5. Sodium carbonate ..	Greenish-blue	Same as bicarbonate colour but changes are more rapid
6. Sodium hydroxide ..	Sudden change to brown	Deep blue; fades fast and becomes pale yellowish-brown

The flavylium salts undergo decomposition slowly on storage and the products become deficient in halogen. This behaviour has been found in the case of many other complex flavylium salts prepared in these laboratories.[6] Due to the presence of water of crystallisation, elimination of halogen acid

seems to take place leading to the formation of colour base or of the chalkone.[7]

Summary

Gossypol condenses with ethylacetoacetate and diethyl malonate in the presence of piperidine to form pyrones and with acetophenone and dihydroxy acetophenone in the presence of hydrogen chloride to form flavylium salts. They are definite crystalline substances with characteristic properties. Thus the presence of two ortho-hydroxyaldehyde groups in the gossypol molecule is established. The dianilino-compound of gossypol also undergoes the above condensations smoothly indicating that it is easily split up into gossypol and aniline under the conditions of the reactions.

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THE MAGNETIC SUSCEPTIBILITY AND ANISOTROPY OF CARBORUNDUM

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1. Introduction

The study of the magne-crystallic behaviour of carborundum should be of considerable interest in view of the fact that the crystal is a valence structure in which the atoms of carbon are bound tetrahedrally to the atoms of silicon and *vice-versa*. Remarkably enough, five crystalline modifications of the substance have been reported, two of which are of the rhombohedral class, two hexagonal and one cubic. According to Moissan, carborundum may be transparent and colourless or vary in tint from emerald green to brown or black. It is not improbable that these variations of colour arise from the presence of impurities in the crystal. If this be the case, they might be expected to affect its magnetic behaviour.

Carborundum was available in Sir C. V. Raman's crystallographic collection in the form of an aggregate in which large crystalline plates had formed out of a matrix. It was possible to break off the crystals and each specimen thus obtained from the matrix was about 5 mm. square in area and a couple of millimeters thick. These crystals were perfectly black, but had smooth and lustrous surfaces. Another sample was also available in the form of a crystalline plate which was translucent and green in colour. This sample had been examined by Dr. C. S. Venkateswaran who found that the Laue pattern given by it with the X-ray beam normal to the plate had hexagonal symmetry. This sample as well as three samples detached from the aggregate were examined for their magnetic behaviour.

The magnetic susceptibility was measured in a Curie balance. A large electromagnet, the coils of which could be clamped at a suitable angle was employed for this purpose. The plates were suspended with the plane parallel to the magnetic field and the susceptibility perpendicular to the hexagonal axis ($\chi_\perp$) was measured by comparison with double distilled water.

The measurements of magnetic anisotropy were made by the torsional method of K. S. Krishnan (1933). A Cook electromagnet with large pole-pieces having an area of 8 cm. × 8 cm. was used and with a pole-gap of 1¼", field strengths of the order of 4000 to 6000 oersted were obtained for moderate currents. A quartz fibre was drawn out in the blast of an oxy-gas flame and used as the suspension. Its torsional constant was determined by the oscillation method with glass cylinders of known moments of inertia and then used for the measurement of the angle of critical torsion. The orientation of the crystal in the magnetic field was determined by the usual method with the help of a telemicroscope mounted on a circular scale and a plane mirror. The non-homogeneity of the field was tested and its effect was found to be negligible. The field was measured with a search-coil and a calibrated fluxmeter.

2. *Results*

The magnetic characteristics of the green plate conformed strictly to the known hexagonal symmetry of the crystal. There was no anisotropy in the plane perpendicular to the hexagonal axis and when suspended with the axis horizontal the orientation of the axis was parallel to the field, showing that χ_{11} was greater than $\chi_{\perp}$ algebraically. Table I gives the experimental data.

TABLE I

Green Hexagonal Plate of Carborundum

Mass of the crystal = 35·0 mgm.

Torsional constant of the fibre = $1{\cdot}429\times10^{-8}$

Field strength	Critical angle of torsion a_c	$(\chi_{11}-\chi_{\perp})$ per gm. mol.
oersted		
4640	357°	$0{\cdot}82_5\times10^{-6}$
5270	446°	$0{\cdot}82_1\times10^{-6}$
5760	526°	$0{\cdot}82_8\times10^{-6}$
6160	597°	$0{\cdot}83_0\times10^{-6}$

Mean = $0{\cdot}82\times10^{-6}$

Since the critical angle of torsion was small, the accurate formula

$$\chi_{11}-\chi_{\perp}=\frac{2c}{m\,H^2}\left(\frac{a_c-\frac{\pi}{4}-\delta}{\cos 2\delta}\right).$$ M., was used where

$$\text{Tan } 2\delta=\frac{1}{2\left(a_c-\frac{\pi}{4}-\delta\right)}$$

The susceptibility was found to be independent of the field strength within the limits of experimental accuracy and a value $-13{\cdot}1 \times 10^{-6}$ per gm. mol. was obtained for $\chi_\perp$.

The deportment of the black crystals in the magnetic field was found to be irregular. All the specimens examined had appreciable anisotropy in the plane perpendicular to the axis. When suspended with the axis horizontal the plates set themselves with their axes at an angle to the field which was different for the different specimens and decreased slowly as the field strength increased. They were found to be diamagnetic but the numerical value of the susceptibility diminished at a rapid rate with the decrease of the magnetic field. Table II gives some experimental data.

TABLE II

Black Crystals of Carborundum

Field strength	$\chi_\perp$ per gm. mol.		
	Crystal I	Crystal II	Crystal III
oersted			
3560	$-5{\cdot}7\times10^{-6}$	$-7{\cdot}5\times10^{-6}$	$-5{\cdot}4\times10^{-6}$
3890	$-6{\cdot}8\times10^{-6}$	$-7{\cdot}9\times10^{-6}$	$-6{\cdot}0\times10^{-6}$
4250	$-7{\cdot}1\times10^{-6}$	$-8{\cdot}2\times10^{-6}$	$-6{\cdot}6\times10^{-6}$

3. *Discussion*

The gm. mol. anisotropy $(\chi_{\parallel} - \chi_\perp)$ obtained for the hexagonal green crystal of carborundum is $0{\cdot}82 \times 10^{-6}$ which is of the same order of magnitude as that for the sulphates and the selenates and much lower than that for the carbonates and the nitrates. In the latter crystals the complexes responsible for their anisotropy retain their characteristics practically unaltered in different compounds and hence the observed susceptibilities can be correlated with the magnetic constants of these complexes. The theory for the interpretation of the feeble diamagnetic anisotropy of crystals having isosthenic lattices is not developed. One example of this type of lattice is quartz which has a gm. mol. anisotropy $(\chi_\perp - \chi_{\parallel})$ of $0{\cdot}12 \times 10^{-6}$. The explanation for the anisotropy of such crystals has to be sought for in the deformation of the electron density distribution of the constituent atoms due to the interaction of their immediate neighbours. The anisotropy of carborundum is greater than that of quartz and this fact is intelligible in view of the fact that its bonds are much stronger and can produce a greater modification of the electron density distribution of the atoms.

The mean of the three principal susceptibilities of the green specimen is $-12{\cdot}8 \times 10^{-6}$ per gm. mol. Only a rough theoretical estimate of its susceptibility is possible. From Slater's expression for the mean square radius of the electron orbits, the susceptibilities of the free carbon and silicon atoms are calculated to be $-9{\cdot}1 \times 10^{-6}$ and $-25{\cdot}1 \times 10^{-6}$ respectively. The experimental value obtained by the author (1944, only the highest value obtained is used) for carbon in the form of diamond is $-0{\cdot}456 \times 10^{-6}$ per gm. which gives a gm. atomic susceptibility of $-5{\cdot}5 \times 10^{-6}$. The value obtained by Honda (1910) for silicon is $-3{\cdot}5 \times 10^{-6}$ and by Owen (1912) is $-3{\cdot}6 \times 10^{-6}$ and these values are much lower than the theoretical value. Assuming an additive law, from the experimental values given above for diamond and carborundum, the susceptibility of silicon is found to be $-7{\cdot}3 \times 10^{-6}$ which is also lower than the theoretical value. Pascal however gets the value -20×10^{-6} for the silicon atom in combination with organic compounds.

In conclusion the author wishes to express his gratitude to Professor Sir C. V. Raman for his keen interest and encouragement in this work.

4. *Summary*

The magnetic susceptibility and anisotropy of carborundum have been measured. The crystals of the black variety examined are found to be diamagnetic but irregular in their behaviour. A green hexagonal plate of carborundum was however found to behave in a regular way. It had a mean gm. mol. susceptibility of $-12{\cdot}8 \times 10^{-6}$ and anisotropy of $0{\cdot}82 \times 10^{-6}$, the susceptibility perpendicular to the hexagonal axis being numerically higher.

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SYNTHESIS OF COMPOUNDS RELATED TO SANTONIN

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Santonin, the lactone of 1-hydroxy-7-keto-8-10-dimethyl $\Delta^{5:8}$-hexahydro-naphthyl-2-propionic acid (A), the well-known naturally occurring anthelmintic, has been recently synthesised by us.[1] The anthelmintic action of santonin is generally attributed to the lactonic and ketonic groups in it. It will be interesting to see whether the methyl groups in 8 and 10 positions in santonin have any marked effect on the anthelmintic action. We have, therefore, synthesised the following compounds related to santonin by the series of reactions given below :—

(1) Lactone of 1-hydroxy-7-keto-$\Delta^{5:8}$ hexahydro naphthyl 2-propionic acid (B).

(2) Lactone of 1-hydroxy-7-keto-8-methyl $\Delta^{5:8}$-hexahydro-naphthyl-2-propionic acid (C).

(3) Lactone of 1-hydroxy-7-keto-10-methyl $\Delta^{5:8}$-hexahydro-naphthyl-2-propionic acid (D).

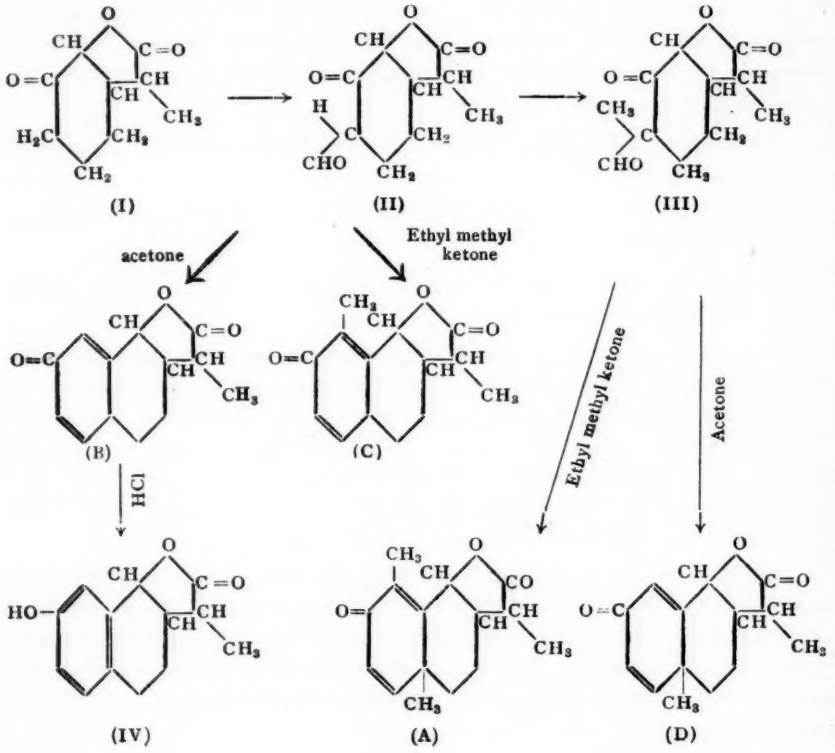
Condensation of 6-keto-2-chloro-Δ^{1}-cyclohexene[3] with diethyl sodio-mono-methyl-malonate, followed by hydrolysis gives the lactone of α-(2-hydroxy-3-keto-cyclohexyl) propionic acid (I). This keto lactone (I) on condensation with ethyl formate in the presence of sodium gives the lactone of α-(2-hydroxy-3-keto-4-formyl-cyclohexyl) propionic acid (II). Condensation of this keto-formyl lactone (II) with acetone and ethyl methyl ketone furnished the lactones (B) and (C) respectively.

The lactone (B) on treatment with fuming hydrochloric acid was converted into the lactone of 1-7-dihydroxy-tetrahydro-naphthyl propionic acid IV, identical with the lactone obtained from 7-methoxy tetralone by Paranjape, Phalnikar and Nargund.[4] It may be noted that the transformation of (B) into (IV) is a reaction analogous to the conversion of santonin into desmotroposantonin.

Condensation of this keto-formyl-lactone (II) with ethyl methyl ketone gave (C). Ethyl methyl ketone may condense with the lactone (II) in two different ways and may give either 8-methyl or 6-methyl lactone. It has been shown by us[1] that ethyl methyl ketone condenses with 2-formyl-cyclohexanone to give 7-keto-8-methyl-hexahydro-naphthalene. On similar lines it is assumed that ethyl methyl ketone will condense with the lactone (II) and give a 8-methyl compound (C) and not the 6-methyl one.

The sodio salt of the lactone (II) when treated with methyl iodide under pressure undergoes methylation and the methylated product (III) when condensed with acetone in the presence of sodium ethoxide gives the lactone (D).

It will be noted that these lactones (B), (C) and (D) differ from santonin in the fact that they contain two or one methyl group less than in santonin. The pharmacological actions of these lactones has been studied and will be reported later.



These compounds contain asymmetric carbon atoms. Details regarding their optical properties will be reported in another communication. A preliminary account of these properties however has been recently published.[2]

Experimental

The preparation of the lactone of α-(2-hydroxy-3-keto-cyclohexyl) propionic acid (I), the lactone of α-(2-hydroxy-3-keto-4-formyl-cyclohexyl) propionic acid (II) and the lactone of α-(2-hydroxy-3-keto-4-formyl-4-methyl cyclohexyl) propionic acid (III) has been described by us.[1]

Lactone of 1-*hydroxy*-7-*keto*-$\Delta^{5:8}$-*hexahydro-naphthyl*-2-*propionic acid* (*B*).—The lactone of α-(2-hydroxy-3-keto-4-formyl-cyclohexyl) propionic acid (II) (8 gm.) was mixed with acetone (2 gm.) and the mixture was added to sodium ethoxide prepared from sodium (3·2 gm.) and absolute alcohol (40 c.c.) and was allowed to stand overnight. Alcohol was then removed on a water-bath and the reaction mixture was acidified with dilute hydrochloric acid and extracted with ether. The ether layer was washed with water, dried over calcium chloride (anhydrous) and ether removed. The residue containing the lactone of 1-hydroxy-7-keto-$\Delta^{5:8}$-hexahydro-naphthyl-propionic acid (B) was a semisolid, which on crystallisation from benzene was obtained as fine needles and melted at 91°.

[Found: C, 71·7; H, 6·5 per cent. Equi. wt. (by back titration), 217·7; $C_{13}H_{14}O_3$ requires C, 71·6; H, 6·4 per cent. and Equi. wt. 218·0.] It gives a semicarbazone, m.p. 145°.

On keeping this lactone with fuming hydrochloric acid in a sealed tube for 21 days, it was transformed into the lactone of 1-7-dihydroxy-tetrahydro-naphthyl propionic acid (IV), m.p. 111° C. identical with the lactone prepared by Paranjape, Phalnikar and Nargund[4] from -7-methoxy-tetralone.

Lactone of 1-*hydroxy*-7-*keto*-8-*methyl*-$\Delta^{5:8}$-*hexahydro-naphthyl*-2-*propionic acid* (*C*):—The lactone (II) was similarly condensed with ethyl methyl ketone in the presence of sodium ethoxide and was worked up as in the above case. The lactone of 1-hydroxy-7-keto-8-methyl-$\Delta^{5:8}$-hexahydro-naphthyl-2-propionic acid (C) thus obtained, crystallised from alcohol and had m.p. 111°.

[Found: C, 72·7; H, 6·9 per cent. Equi. wt. (by back titration), 232·1; $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9 per cent. and Equi. wt. 232·0.]

Lactone of 1-*hydroxy*-7-*keto*-10-*methyl*-$\Delta^{5:8}$-*hexahydro-naphthyl*-2-*propionic acid* (*D*).—Condensation of the lactone of α-(2-hydroxy-3-keto-4-formyl-4-methyl cyclohexyl)-propionic acid (III) with acetone was carried out as

in the above case. The lactone of 1-hydroxy-7-keto-10-methyl-$\Delta^{5:8}$-hexahydro-naphthyl-2-propionic acid (D) was first obtained as a syrupy liquid but on purification and crystallisation from alcohol it was obtained as a solid, m.p. 141°. It gave a semicarbazone, m.p. 201° C.

[Found: C, 72·8; H, 6·9 per cent. and Equi. wt. (by back titration), 231·8; $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9 per cent. and Equi. wt. 232·0.]

Summary

Following the methods used in the synthesis of santonin the synthesis of compounds related to santonin has been described.

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SYNTHESIS OF CANTHARIDINE AND DESOXYCANTHARIDINE

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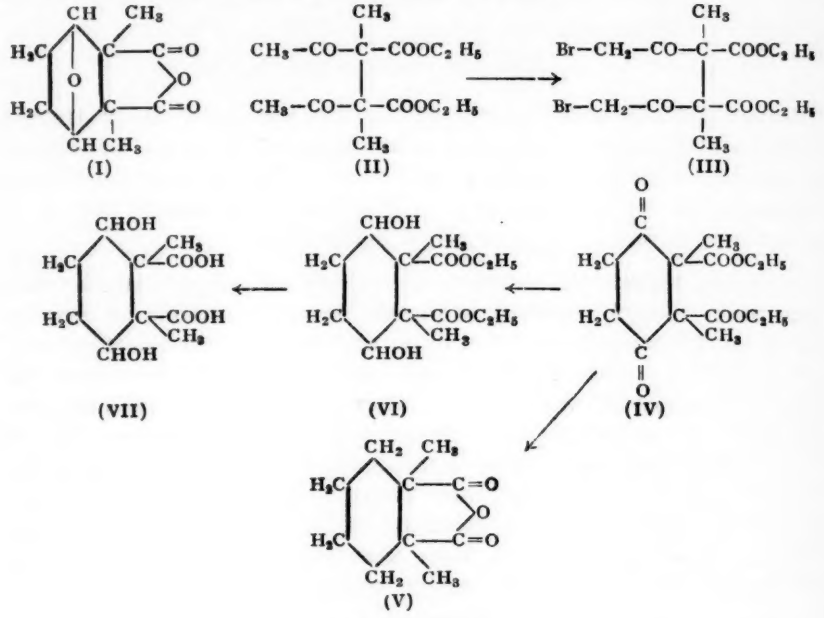
Cantharidine, the active principle of *Cantharis vesicatoria*[1] and of *Mylabris pustulata* Fb. India[2] has been assigned the structure (I) mainly on the basis of analytical evidence by Gadamer and others.[3] This structure has received further support by the observation of Bruchhausen and Bersch[4] that maleic anhydride is formed in the pyrolysis of cantharidine.

Various unsuccessful attempts at the synthesis of cantharidine have been made. Steele[5] attempted to prepare desoxycantharidine by debrominating $\alpha\alpha'$-dibromo-$\alpha\alpha'$-dimethyl suberic acid but the debromination could not be effected. Guha and Iyer[2] unsuccessfully attempted to replace bromine by cyanogen in 1-2-dibromo-1-2-dimethyl-cyclohexane. Pai and Guha[6] attempted to methylate 3-6-diketo-cyclohexane-1-2-dicarboxylate but no C methylation took place. The condensation of ethyl $\beta:\beta'$-diketo-tetrahydrofuran-$\alpha\alpha'$-dicarboxylate either with ethyl-α-bromo propionate or with alkylene bromides proved unsuccessful.[7] Diels and Alder[8] failed to add dimethyl maleic anhydride to furan although nor-cantharidine and iso-cantharidine were prepared by similar methods.

Recently Woodward and Loftfield[9] have reported the synthesis of desoxycantharidine by the reduction of the addition product obtained from butadiene and dimethyl maleic anhydride. Ziegler, Schenck, Krockow, Siebert, Wenz and Weber[10] have reported the synthesis of cantharidine and desoxycantharidine by a series of long and difficult reactions. The present paper describes the synthesis of these substances by a simpler method.

Sodio derivative of ethyl-α-methyl-acetoacetate when treated with iodine gave diethyl-$\alpha\alpha'$-diacetyl-$\alpha\alpha'$-dimethyl succinate (II). Bromination of (II) gave the dibromo-compound (III), which on treatment with finely divided silver was debrominated and cyclised to diethyl-3-6-diketo-1-2-dimethyl cyclohexane-1-2-dicarboxylate (IV). Clemmenson reduction of (IV) followed by hydrolysis and steam distillation gave desoxycantharidine (V). Reduction

of (IV) by aluminium isopropoxide gave (VI) which on hydrolysis gave the corresponding dihydroxy acid (VII). Treatment of crude (VI) with concentrated sulphuric acid at room temperature for 100 hours gave a black mass from which cantharidine was obtained by sublimation. The synthetic sample of cantharidine had m.p. 217° C. and did not depress the m.p. of an authentic sample kindly supplied by Dr. P. C. Guha, Indian Institute of Science, Bangalore, to whom our thanks are due.



Experimental

Diethyl-αα'-diacetyl-αα'-dimethyl succinate (*II*).—To finely pulverised sodium (4·6 gm.) suspended in dry benzene (50 c.c.) was added ethyl-α-methyl-acetoacetate (28·8 gm.). It was then refluxed for three hours and iodine (25·4 gm.) was then added and refluxing continued till the colour of iodine disappeared. It was then treated with ice and dilute sulphuric acid. The benzene layer was separated, washed with water and dried and benzene was removed. The residue could not be purified by distillation under reduced pressure and was therefore used to prepare the bromo-compound as described below.

Diethyl-αα'-di-(ω-bromoacetyl)-αα'-dimethyl succinate (*III*).—To a solution of the above ester (II) (28·6 gm.) in carbon disulphide (50 c.c.) was

added bromine (32 gm.) dissolved in the same solvent (50 c.c.), a trace of anhydrous aluminium chloride being used as a catalyst. Vigorous evolution of hydrobromic acid took place. The residue after removal of carbon disulphide was crystallised from benzene and had m.p. 55° C.

[Found: Br, 36·4; $C_{14}H_{20}O_6Br_2$ requires Br, 36·0%.]

Diethyl-3-6-*diketo*-1-2-*dimethyl-cyclohexane*-1-2-*dicarboxylate* (*IV*).—Diethyl-$\alpha\alpha'$-di-(ω-bromoacetyl)-$\alpha\alpha'$-dimethyl succinate (III) (22 gm.) and molecular silver (10·8 gm.) were heated together on an oil-bath at 120° C. for three hours and then at 150° C. for half an hour. The product recovered by ether extraction was a viscous liquid which could not be distilled without decomposition. It was characterised by its di-*p*-nitrophenyl hydrazone, m.p. 143° C.

[Found: C, 56·2; H, 5·4; N, 15·6. $C_{26}H_{30}N_6O_8$ requires C, 56·3; H, 5·4; N, 15·2%.]

1-2-*Dimethylcyclohexane*-1-2-*dicarboxylic anhydride* (*V*).—Diethyl-3-6-diketo-1-2-dimethylcyclohexane-1-2-dicarboxylate (IV) (5 gm.) was reduced by zinc amalgam by Clemmenson's method. The product recovered by ether extraction was hydrolysed by alkali and the product obtained after acidification was steam-distilled. The steam volatile product was identified as desoxycantharidine, m.p. 128°. The steam-non-volatile product crystallised from alcohol when it had m.p. 165°. It was therefore 1-2-dimethyl cyclohexane dicarboxylic acid.

[Found: C, 60·3%; H, 8·0% and Eq. wt. 100·4. $C_{10}H_{16}O_4$ requires C, 60·0%; H, 8·0%; Eq. wt. 100.] Woodward and Loftfield[9] give m.p. 129° for desoxycantharidine and m.p. 166° for desoxycantharic acid.

3-6-*Dihydroxy*-1-2-*dimethylcyclohexane*-1-2-*dicarboxylic acid* (*VII*).—Diethyl 3-6-diketo-1-2-dimethylcyclohexane 1-2-dicarboxylate (IV) (15·2 gm.) was reduced by aluminium isopropoxide (from aluminium 0·8 gm. and isopropyl alcohol 34 c.c.) following the method of Lund.[11] The recovered product (VI) was directly hydrolysed by alkali and the acid obtained when crystallised from petrol, had m.p. 99°.

[Found: C, 51·92%; H, 7% and Eq. wt. 116·2. $C_{10}H_{16}O_6$ requires C, 51·72%; H, 6·89% and Eq. wt. 116.] It was soluble in all organic solvents except chloroform.

3-6-*Oxido*-1-2-*dimethyl-cyclohexane*-1-2-*dicarboxylic anhydride* (*Cantharidine*) (*I*).—Crude diethyl-1-3-6-dihydroxy-1-2-dimethyl-cyclohexane 1-2-dicarboxylate (VI) (10 gm.) obtained in the above experiment, was mixed with concentrated sulphuric acid (100 gm.) and the mixture was kept at room

temperature for 100 hours. It was then poured into water and the product recovered by ether extraction was hydrolysed by alkali. It was then acidified and extracted with chloroform. The product obtained after removal of chloroform was sublimed preferably with a drop of concentrated sulphuric acid when cantharidine was obtained in colourless needles, m.p. 217° and did not depress the m.p. of an authentic specimen. It gave all the colour reactions of cantharidine (yield 10% calculated on ethyl acetoacetate used).

[Found: C, 61·3%; H, 6·1%. $C_{10}H_{12}O_4$ requires C, 61·2%; H, 6·1%.] It formed a mono-phenyl-hydrazone, m.p. 193 (*cf.* Spiegel[12]).

Summary

A new and simple method for the synthesis of cantharidine and desoxy-cantharidine has been described.

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OPACITY CHANGES DURING THE COAGULATION OF SOLS BY ELECTROLYTES

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The opacity method of following the coagulation of a sol was first developed by Mukherjee and Mujumdar[1] by allowing the light transmitted through the coagulating system to fall on a thermopile connected to a galvanometer. Desai[2] modified this method by using a photo-cell in place of thermopile. Prasad and Modak[3] modified Desai's method by amplifying the current from the photo-cell. Recently, Prasad and Gogate[4] have designed an apparatus for the measurement of opacity of gel-forming systems and they find that results of fairly high repetibility can be obtained by the use of this apparatus. This was therefore used to study the kinetics of coagulation of sols by electrolytes, and the effects of temperature and the addition of non-electrolytes on the coagulation were also examined. The sols employed were those of thorium, stannic, and zirconium hydroxides; the coagulation of some of these has been studied previously by some workers. The results obtained are discussed in the following pages.

1. Results and Discussion

(*a*) *Thorium hydroxide sol.*—The sol was prepared by the method adopted by Desai (*loc. cit.*), and was dialysed for 7 days. The concentration of the sol was found to be 4·1 g. of ThO_2 per litre.

Equal volumes of the sol and electrolytes (K_2SO_4, KCl, KNO_3, $BaCl_2$, NaCl) of different concentrations were mixed and the opacity of the coagulating mixture was measured at different intervals of time commencing from the time of mixing. The time-deflection curves obtained during the coagulation of the sol by the highest and lowest concentrations employed are shown graphically in Figs. 1 and 2. The concentrations of the electrolytes mentioned refer to the amounts of electrolytes present in the total volume (9 c.c.) of the coagulating mixture.

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* Springer Research Scholar of the Bombay University.

[1] *J. C. S.*, 1924, 125, 785.

[2] *Trans. Farad. Soc.*, 1928, **24**, 181.

[3] *Proc. Ind. Acad. Sci.*, 1940, **12**, 235.

[4] *Ibid.*, 1943, **17**, 163.

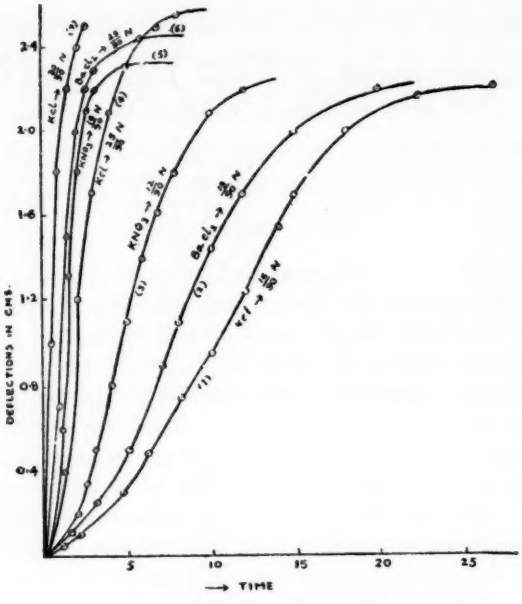


FIG. 1. Coagulation of Thorium Hydroxide Sol.

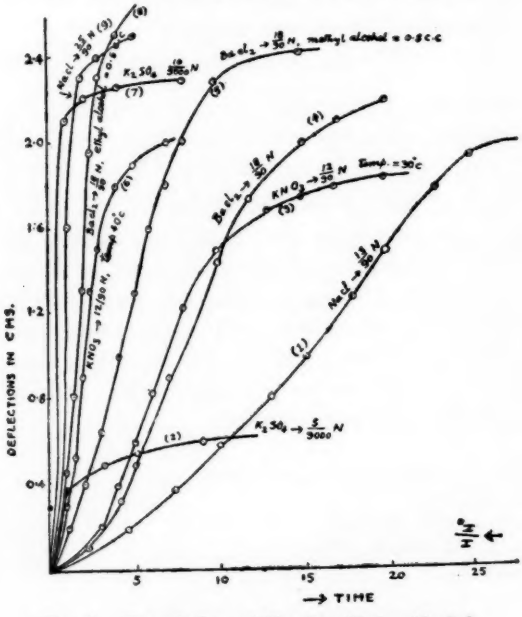


FIG. 2. Coagulation of Thorium Hydroxide Sol.

All the curves in Figs. 1 and 2 are continuous showing thereby that coagulation is a continuous phenomenon. Potassium sulphate is a good coagulator (*cf.* curves 2 and 7, Fig. 2) since its concentration required for coagulation is relatively smaller than those of other electrolytes. This may be due to the bivalent nature of the coagulating ion. Moreover, the coagulation in the presence of potassium sulphate is rapid, it being nearly completed in about 2 minutes in the presence of 1/900 N K_2SO_4; if its concentration is less than this only partial coagulation takes place.

The behaviour of the other electrolytes is very similar to each other but different from that of potassium sulphate. The coagulation of the sol by barium chloride in the presence of ethyl and methyl alcohols shows that the rate of coagulation is greatly increased by such an addition (*cf.* curves 4, 5 and 8, Fig. 2), the increase being greater in the presence of ethyl than methyl alcohol.

Temperature has a great effect on the coagulation velocity (*cf.* curves 3 and 6, Fig. 2). The rate of coagulation is accelerated by the increase in temperature, but the nature of the curves remains the same.

The observations for the same sol taken at 30° with 12/90 N potassium nitrate given in Fig. 2 (curve 3) differ from those given in Fig. 1 (curve 3); the former were taken about a month after the latter. The observed differences are apparently due to the ageing of the sol during this period.

An examination of the various curves in Figs. 1 and 2 shows that the final value of opacity in the presence of different amounts of the same electrolyte is not the same. Usually it increases, though slightly, when increasing amounts of the electrolytes are added. This increase is also noticeable when the sol is coagulated at different temperatures and in the presence of ethyl and methyl alcohols. These changes are predominant in the coagulation of the sol by potassium sulphate. A comparison of the curves obtained with a freshly prepared sol and the one which has aged for a month shows that the final value of opacity in the case of the aged sol is less than that in the fresh one. The above-mentioned differences may have been caused by a number of factors which come into play during and immediately after the process of coagulation.

The coagulating power of an electrolyte is the reciprocal of the minimum concentration of the electrolyte required to effect a definite stage of coalescence (from the first appearance of turbidity to complete separation of the coagulum) in a given time. The results obtained in this investigation can be used to compare accurately the coagulating powers of the electrolytes employed for the coagulation of the sol since the measurements of

opacity give fairly high reproducible and accurate results. For this purpose curves were drawn between the time required for the coagulating mixture to attain a certain value of opacity (deflection of 1 cm.) against concentrations of several electrolytes used for coagulation. It is found from these curves that the concentrations of the different electrolytes necessary to cause coagulation in a given time follow the following descending order KNO_3> NaCl>KCl>$BaCl_2$. Hence the descending order of coagulating power of these electrolytes is KNO_3>NaCl>KCl>$BaCl_2$. For a time equal to 2 minutes the coagulating powers are KNO_3: NaCl : KCl: $BaCl_2$= 1·76: 1·17: 1·07: 1·00.

(*b*) *Stannic hydroxide sol.*—This sol was prepared by the same method as adopted by Dhar and Vardhanam.[5] Three samples of the sol were employed for coagulation experiments: (A) undialysed sol, (B) sol dialysed for 8 days and (C) sol dialysed for 15 days. The colloidal contents of the three samples of the sol were 33·1, 17·4 and 13·9 g. of SnO_2 per litre.

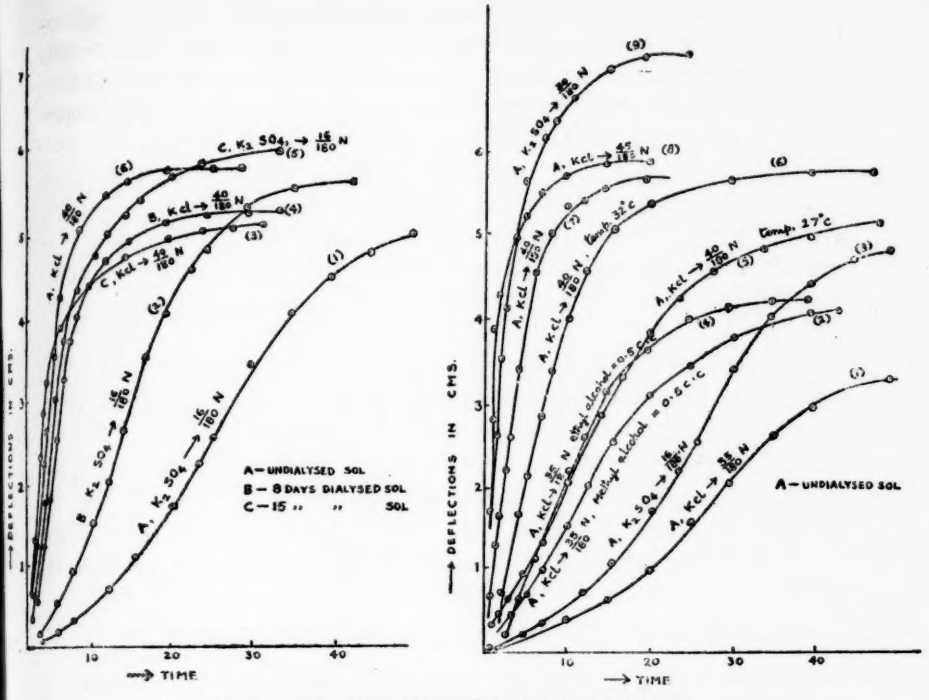
The experimental procedure followed was exactly the same as that adopted in the case of thorium hydroxide sol.

Some of the results obtained are graphically shown in Figs. 3 and 4. It will be seen in this case also that all the curves are continuous thereby showing that coagulation is a continuous phenomenon. Most of the curves are 'S' shaped while some of them are steep rising ones.

The coagulating power of the electrolytes employed for coagulation of this sol was compared by the same method as used in the case of thorium hydroxide sol and it was found that the coagulating power of potassium sulphate is greater than that of potassium chloride for all the three samples. This may be due to the bivalent nature of the coagulating ion in potassium sulphate. Moreover it appears from the large differences in opacity that the coagulation in the presence of potassium sulphate is more complete than that by potassium chloride. Further, it will be observed that the rate of change and the final values of opacity increase as the amount of the coagulating electrolyte increases. The coagulating powers of the two clectrolytes for deflection equal to 2 cm. and time 10 minutes is K_2SO_4: KCl = 1·88: 1·00.

The coagulation by potassium chloride of the three samples of the sol in the presence of ethyl and methyl alcohols has been investigated. A comparison of the curves 1 and 4, 1 and 2, Fig. 3, for undialysed sample shows that the rate of coagulation is accelerated by the presence of alcohols

[5] *J. Indian Chem. Soc.*, 1936, **13**, 602.



FIGS. 3 and 4. Coagulation of Stannic Hydroxide Sol.

and that the effect of ethyl (curves 1 and 4) is greater than that of methyl (curves 1 and 2) alcohol. The effect of these alcohols on the other two samples is also of the same nature as on the undialysed sol.

Temperature increases the rate of coagulation (curves 5 and 6, Fig. 3). This observation is similar to that for thorium hydroxide sol (curves 3 and 6, Fig. 2).

The coagulation by the same concentration of KCl and K_2SO_4 of sols (A), (B) and (C) is graphically shown in Fig. 4. The effect of dialysis on the coagulation of the sol by the same concentration of electrolytes cannot be well compared because the amount of colloidal matter in the three samples is not the same; it has been found to decrease as dialysis is continued. The curves in Fig. 4 show that the rate of change of opacity and the final values of opacity increase on dialysis when the sol is coagulated by potassium sulphate (curves 1, 2 and 5) and decrease when potassium choride (curves 6, 4 and 3) is used as the coagulator; they thus point out the specific nature of the action of the coagulating electrolyte.

(*c*) *Zirconium hydroxide sol.*—The method employed for the preparation of this sol was the same as that used by Sharma and Dhar.[6] Two samples of the sol were employed for coagulation experiments: sol dialysed for 20 days (A) and 30 days (B). The concentrations of the two samples were 6·5 and 5·0 g. ZrO_2 per litre, respectively.

The results obtained are shown graphically in Fig. 5. The continuous nature of the curves points to the continuous nature of the coagulating process. It will be seen from the various curves in Fig. 5, that the rate of coagulation, as indicated by the rate of change of opacity, and the final values of opacity increase as larger amounts of electrolytes are used for coagulation.

The effect of dialysis on the coagulation of this sol also cannot be well compared as the concentrations of the differently dialysed sol are not the same. However, it can be said that the amount of electrolyte necessary for coagulation decreases as the sol is further dialysed (*cf.* curves 1 and 6, Fig. 5).

The effect of temperature is brought out by curves 3 and 5, Fig. 5. Temperature accelerates coagulation. The effect of alcohols on coagulation by electrolytes of this sol is the same as that for other sols investigated, namely, it increases the rate of coagulation (*cf.* curves 4 and 8, Fig. 5).

2. Explanation of the Observed Results on Smoluchowski's Theory

Smoluchowski has developed a theory of rapid coagulation velocity on the assumptions that (1) round each discharged particle there exists a sphere of attraction of radius r and (2) if two particles approach during molecular motion so closely that the centre of one enters the sphere of attraction of the other they would remain adherent. According to this theory the total number of particles Σv at any time t is given by $v_0(1+t/\theta)$, where v_0 is the number of single particles originally present in the sol and $\theta = Kv_0$, the specific coagulation time, is a constant. The number of single, double, triple, etc., particles at any time is given by the following relations:

$$v_1 = \frac{v_0}{\left(1+\frac{t}{\theta}\right)^2}\ ;\quad v_2 = \frac{v_0\cdot\frac{t}{\theta}}{\left(1+\frac{t}{\theta}\right)^3};\quad v_3 = \frac{v_0\left(\frac{t}{\theta}\right)^2}{\left(1+\frac{t}{\theta}\right)^4}\quad \ldots$$

$$v_n = \frac{v_0\left(\frac{t}{\theta}\right)^{n-1}}{\left(1+\frac{t}{\theta}\right)^{n+1}}$$

[6] *Ibid.*, 1932, **9**, 455.

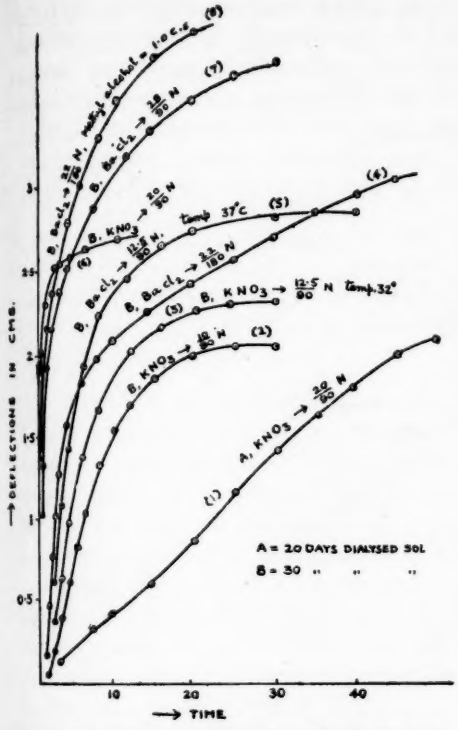

DEFLECTIONS IN CMS.
TIME
A = 20 DAYS DIALYSED SOL
B = 30 " " "
A. KNO3 → 20/80 N
B. KNO3 → 12·5/80 N Temp. 32°
B. KNO3 → 20/80 N Temp. 37°C
B. Ba Cl2 → 2·5/80 N
B. Ba Cl2 → 2·5/160 N
B. Ba Cl2 → 2·5/80 N, methyl alcohol = 1·0 c.c.

FIG. 5. Coagulation of Zirconium Hydroxide Sol

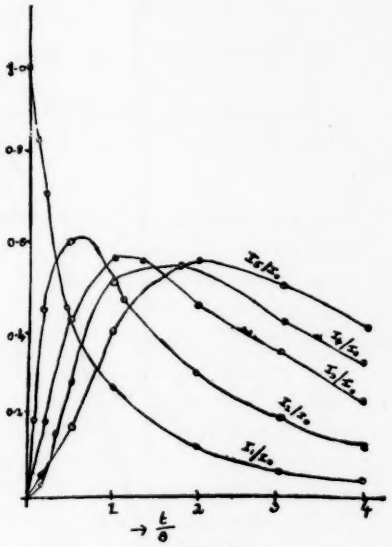


FIG. 6

The intensity of light scattered transversely by a colloidal system consisting of N particles of size V is proportional to NV^2 provided the diameter of the particles is less than the wavelength of light. The diameter of the colloidal particles varies from 1–100 $\mu\mu$; taking the upper limit for the particle size, it is apparent that the law (Rayleigh) will hold true for the coalescence of a large number of particles. The intensity of light transversely scattered (I_1, I_2, I_3, etc.) by single, double, triple, etc., particles of twice, thrice, etc., the volume of the single particles, will be given by the following relations:

$$I_1 = \frac{I_0}{\left(1+\frac{t}{\theta}\right)^2}; \quad I_2 = \frac{4\,I_0\,\frac{t}{\theta}}{\left(1+\frac{t}{\theta}\right)^3}; \quad I_3 = \frac{9\,I_0\left(\frac{t}{\theta}\right)^2}{\left(1+\frac{t}{\theta}\right)^4}$$

and so on

where $I_0 = kv_0V^2$, V being the volume of the single particles.

The variation of I_1/I_0, I_2/I_0, I_3/I_0, etc., with different intervals of t/θ is shown in Fig. 6. It will be seen that the scattering due to single particles steadily decreases whereas that due to double and multiple particles at first increases, reaches a maximum value, and then falls off. At any instant, the total scattering will be the sum of I_1/I_0, I_2/I_0, I_3/I_0, etc. The variation of $\Sigma I/I_0$

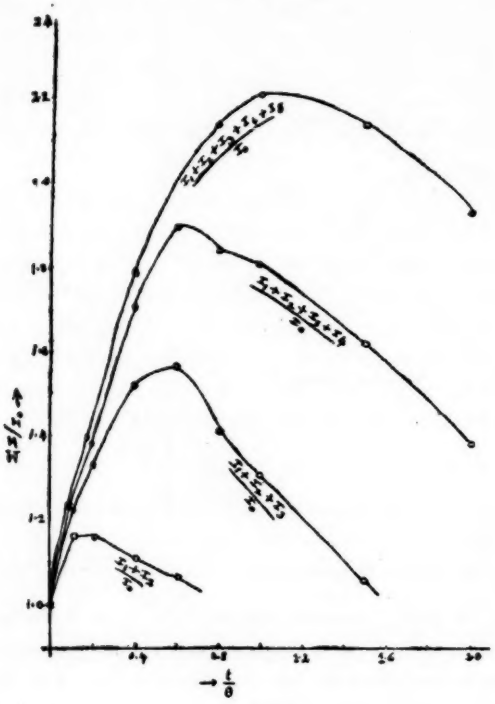


FIG. 7.

with t/θ is given in Fig. 7. It will be seen that $\Sigma I/I_0$ increases with time, reaches a maximum value and then begins to decrease. The time taken to reach the maximum value increases as the particles of greater multiplicity are formed when the intensity of scattered light also increases more rapidly with time.

According to Smoluchowski the kinetics of slow coagulation is the same as that for rapid; only in the case of slow coagulation the " adherence factor " is less than one. Hence $\Sigma I/I_0$–t curves for slow coagulation must be the same as that for rapid.

The opacity-time curves during the coagulation of sols represent roughly the variation of the intensity of scattered light with time. The similarity of the curves in Fig. 7 with those rapidly rising curves in Figs. 1 to 5 explains the results in this investigation. The "S" shaped opacity-time curves obtained for slow coagulation show that the assumption of Smoluchowski, namely, that the kinetics of slow coagulation is the same as that for rapid coagulation may not be true.

3. *Verification of Smoluchowski's Equation from Opacity Data*

The opacity data obtained can be employed to examine the applicability of Smoluchowski's equation to the coagulation of the sols studied in this investigation.

According to Smoluchowski Σv, the total number of particles (single, double, triple, etc.) at a time t is given by $v_0/(1 + t/\theta)$ as stated before and the stages of coalescence are independent of the external conditions which can change only the rapidity of succession of these stages. According to Mukherjee and Papaconstantinou[7] any property that varies continuously with the progress of coalescence without having a maxima or minima can be utilised to characterise the stages of coalescence, for each value of this property is characteristic of the time that has elapsed since the mixing of the electrolyte and the sol. Hence the coagulation velocity curves with the same electrolyte of different concentrations must be related to each other; that is, the values of the ratios of T_1/T, T_2/T, T_3/T, etc., must be the same for all concentrations of the same electrolyte (T, T_1, T_2, T_3, etc., being the respective times taken to reach the same stage of coalescence with an electrolyte of concentrations C, C_1, C_2, etc.).

Assuming that the opacity measurements correctly represent the different stages of coalescence, the values of T, T_1, T_2, T_3, etc., were read from the opacity-time curves obtained with different electrolytes of several concentrations in the case of sols studied in this investigation and the results obtained are given in Tables I to III, in which the different stages of coalescence are represented by opacity (d) of the coagulating mixture.

It will be seen from the results that the values of T_n/T are fairly constant at higher concentrations and as the concentrations of the electrolytes are reduced, there are variations in the value of T_n/T, which shows definitely that the equation is applicable only upto a certain stage of coagulating

[7] *Phil. Mag.*, 1922, **44**, 305.

TABLE I

Thorium hydroxide sol

Values of T_π/T for various electrolytes

(*a*) *Barium chloride*

d.	25/90 N	22/90 N	20/90 N	18/90 N
cm.				
0·7	1	2·5	3·3	6·0
1·5	1	2·5	4·0	7·2
2·0	1	2·5	4·3	7·5
2·2	1	2·5	4·0	8·0

(*b*) *Potassium chloride*

d.	30/90 N	25/90 N	22/90 N	20/90 N	18/90 N	16/90 N
cm.						
1·0	1	3·5	4·2	8·0	16·0	20·8
1·8	1	3·3	4·6	7·0	11·8	16·0
2·2	1	3·1	4·6	6·6	10·0	13·3

(*c*) *Potassium nitrate*

d.	16/90 N	15/90N	14/90 N	13/90 N	12/90 N
cm.					
0·6	1	1·2	1·7	2·3	3·4
1·3	1	1·1	1·8	3·0	3·6
1·8	1	1·2	2·0	3·2	4·0
2·1	1	1·6	2·4	3·6	4·0

(*d*) *Sodium chloride*

d.	25/90 N	20/90 N	17/90 N	15/90 N	13/90 N
cm.					
1·6	1	4·3	9·0	10·3	21·0
1·9	1	4·4	8·8	11·2	19·2
2·1	1	4·3	8·7	11·3	..

TABLE II

Stannic hydroxide sol

Values of T_n/T for different electrolytes

(*a*) *Potassium chloride*

d.	45/180 N	40/180 N	37·5/180 N	35/180 N
cm.				
1·7	1	2·7	10·0	34·8
2·8	1	3·0	10·0	37·0
3·5	1	2·9	9·5	..

(*b*) *Potassium sulphate*

d.	30/180 N	26/180 N	20/180 N	16/180 N
cm.				
1·6	1	4·0	10·5	18·5
3·5	1	3·3	9·5	15·5
4·6	1	3·0	9·0	14·3
5·2	1	2·6	8·0	..

TABLE III

Zirconium hydroxide sol

(*a*) *Barium chloride*

d.	28/180 N	25/180 N	22/180 N
cm.			
1·3	1	2·0	3·0
1·9	1	2·0	4·0
2·1	1	2·0	5·0
2·5	1	1·5	6·2
3·0	1	1·1	4·0

(*b*) *Potassium nitrate*

d.	40/180 N	30/180 N	20/180 N
cm.			
1·6	1	3·0	20·0
2·1	1	3·3	33·0

concentrations. This conclusion is in good agreement with those obtained by previous workers.

Summary

The changes in opacity during the coagulation of (*a*) thorium hydroxide, (*b*) stannic hydroxide and (*c*) zirconium hydroxide sols have been investigated. The results have been used to compare the coagulating power of electrolytes and also to study the applicability of Smoluchowski's equation to the coagulation of these sols. It has been found that Smoluchowski's equation is applicable upto a certain stage of coagulator concentrations only (corresponding to rapid coagulation). The effect of temperature and the influence of alcohols have also been studied. Both these factors accelerate the rate of coagulation in the case of all the sols investigated.

Basing on the theory of Smoluchowski for rapid coagulation an attempt has been made to follow theoretically the changes in the intensity of light scattered transversely (I) by a system undergoing coagulation. The opacity-time curves obtained during the coagulation of sols have been compared with I–T curves obtained theoretically. The curves experimentally obtained for rapid coagulation are similar to those theoretically deduced. However the I–*t* curves for slow coagulation are "S" shaped and it has been inferred that Smoluchowski's equation is not applicable in the region of slow coagulation. This conclusion is the same as that obtained from the direct verification of Smoluchowski's equation from the opacity data.

FLUORESCENCE REACTIONS WITH BORIC ACID AND *O*-HYDROXY-CARBONYL COMPOUNDS, AND THEIR APPLICATION IN ANALYTICAL CHEMISTRY

Part III. Effect of Bromination of the *O*-Hydroxy-Carbonyl Molecule on the Appearance of Fluorescence Effects with Boric Acid

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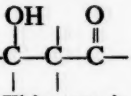
Received March 28, 1944

In a previous communication[1] Neelakantam, Row and Venkateswarlu suggested a new fluorescence reaction for the detection of the  group in aromatic compounds containing C, H and O only. This test is carried out by dissolving the substance in concentrated sulphuric acid, diluting with more acid if the solution is coloured and then adding boric acid to one half of the solution, leaving the other half for blank test. The solutions placed in quartz test-tubes are examined for fluorescence effects produced on adding boric acid, *viz.*, (*a*) appearance of fluorescence if the blank is non-fluorescent, and (*b*) an increase in intensity or (*c*) a change in colour of the fluorescence when the blank is itself fluorescent. Observations are made both in daylight and under ultra-violet light using the Cenco Black Light Source described as argon-filled gas glow lamp fitted with U.V. Filter.[2] If the results are positive, except in the case of the simple 3 hydroxy-flavones (*loc. cit.*), it could be deduced that the molecule contained the *O*-hydroxy-carbonyl group while negative results using this lamp, which is a very poor source of ultra-violet light, though cheap and readily handled, did not necessarily indicate the absence of this group. This reaction has been shown to be more general and of greater applicability, not being confined to any one type of compounds, than any other reaction previously reported in the literature. It is, therefore, of considerable interest to investigate the effect of introducing groups and atoms such as the sulphonic, nitro, amino and halogens into the molecule of the *O*-hydroxy-carbonyl compound on the applicability of this reaction.

Neelakantam and Row[3] pointed out that sulphonation of the *O*-hydroxy-carbonyl compound generally produced a marked increase in the intensity

of fluorescence while nitration and bromination damped the fluorescence considerably and in the cases examined the latter two caused the disappearance of fluorescence. Thus 5-nitrosalicylic acid and nitro-sulphosalicylic acid did not exhibit any fluorescence effects with or without boric acid in daylight or under the lamp while salicylic acid gave prominent effects with boric acid under the lamp, and with sulphosalicylic acid the effects were relatively more prominent. 5-Bromosalicylaldehyde, the only bromo com-

Compound	Under U.-V. Lamp		Remarks
	Without boric acid	With boric acid	
1. 3 : 5-Dibromo-resaceto-phenone	Nil	Greenish yellow	Resacetophenone—bright blue with boric acid under lamp ; blank nil
2. 2-Hydroxy-4-methoxy-5-bromo-benzaldehyde	Nil	do.	2-Hydroxy-4-methoxy-benzal-dehyde—greenish yellow with boric acid under lamp ; blank nil
3. 2-Hydroxy-4-methoxy-3 : 5-dibromo-benzaldehyde	Nil	Nil	
4. 2 : 4-Dihydroxy-3 : 5-di-bromobenzaldehyde	Nil	Nil	β-Resorcylic aldehyde—green with boric acid under lamp ; blank nil
5. 3 : 5-Dibromo-resorcylic acid	Nil	Pale blue	β-Resorcylic acid—bright violet with boric acid under lamp ; blank nil
6. Do. Methyl ester ..	Nil	do.	
7. 3 : 5-Dibromo-orsellinic acid-ethyl ester	Nil	do.	Orsellinic acid and ethyl or-sellinate—deep violet with
*8. Do. Methyl ester ..	Nil	do.	boric acid under lamp ; blank nil
9. 3 :5-Dibromo-orsellinic acid	Nil	do.	
10. 3 : 5-Dibromo-orc-aceto phenone	Nil	Pale yellow	
11. 3 : 5-Dibromo-orcylic aldehyde	Nil	Nil	Orcylic aldehyde—bright greenish yellow with boric acid under the lamp ; blank nil
12. 3 : 5-Dibromo-2 : 4 : 4′-tri-hydroxy-3′-methoxy-chalkone	Nil	Pale yellow	2 : 4 : 4′-trihydroxy-3′-methoxy-chalkone—yellow with boric acid under lamp ; blank nil
13. 3 : 5-Dibromo-6-methyl-2 : 4 : 4′-trihydroxy-3′-methoxy-chalkone	Nil	Nil	
14. 3 : 5-Dibromo-2 : 4-dihydroxy-chalkone	Pale yellow	Deeper yellow	2 : 4-Dihydroxy-chalkone—pale greenish yellow in blank and deeper greenish yellow under the lamp
15. 3 : 5-Dibromo-2 : 4-di-hydroxy-4′-methoxy-chalkone	do.	do.	

*Compounds 8 to 15 were recently synthesised by Seshadri and Venkateswarlu—unpublished work.

pound then examined, showed that introduction of bromine into salicylaldehyde led to complete disappearance of fluorescence effects with boric acid while salicylaldehyde itself gave a positive reaction. Further it was found that bromide interfered with the resacetophenone—boric acid reaction using concentrated sulphuric acid and the explanation was offered that this was due to the production of bromine and bromination of resacetophenone.[4]

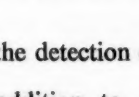
The bathofloric effect of halogens on fluorescence of organic compounds is well known.[5] Thus fluorescein is much more fluorescent than eosin, erythrosin and Rose-Bengal which are its brominated, iodinated and chlorinated derivatives. The ability of free halogens to inhibit (or quench) the fluorescence of fluorescein is a well-known reaction for the detection of the halogen, especially bromide in presence of large amounts of chloride[6] and also iodide. The object of the present investigation, however, is to find out the effect of introducing one or more halogen atoms, *e.g.*, bromine, into the molecule of an *O*-hydroxy-carbonyl compound on the "boric acid reaction". It may be pointed out that this investigation is not concerned with the differences in fluorescence of the parent compound and its halogen derivative but with the effect of adding boric acid to the latter.

Experimental

The solutions were prepared and the tests carried out exactly as described in the previous communications. With none of the compounds examined was any fluorescence observed with or without boric acid in daylight. In the following table, therefore, the results obtained under the lamp and the colour of the fluorescence are reported. For comparison the results previously reported with the bromine-free compounds are given under remarks.

Discussion

It may be stated in general that the fluorescence effects obtained were much less marked in the case of the bromo-compounds than with the corresponding halogen-free compounds. Consequently care must be exercised in the interpretation of the results obtained. It must be emphasised in this connection that the lamp used is a very weak source of U.-V. light and the filter provided with the lamp transmits a little in the violet-blue region. Further it was observed that some samples of boric acid dissolved in concentrated sulphuric acid showed a very faint blue fluorescence. These, however, were of little significance when the bromine-free compounds were examined as the effects were prominent but could not be disregarded in the present investigation. Careful testing with the aid of blanks showed that there was an increase in intensity of fluorescence on the addition of boric acid

in several cases given in the table. From the results now reported taken in conjunction with those previously published it could be deduced that the introduction of bromine atoms into the molecule of an *O*-hydroxy-carbonyl compound does not invariably lead to complete disappearance of fluorescence effects with boric acid and though there is a marked diminution of intensity. The results depend on the nature of the compound and the number of bromine atoms introduced. From this it is clear that the boric acid reaction serves for the detection of the  group in compounds containing bromine in addition to C, H and O. However it must be pointed out that negative results with boric acid are obtained more often when bomine is present than in its absence. Attention may be drawn in this connection to the fact recorded in the previous paper that a negative fluorescence reaction with boric acid using the Cenco lamp as the source of U.-V. light does not necessarily indicate the absence of the *O*-hydroxy-carbonyl group.

Conclusion

The introduction of bromine atoms into the molecule of an *O*-hydroxy-carbonyl compound does not invariably result in absence of fluorescence effects on the addition of boric acid.

The fluorescence test for the *O*-hydroxy-carbonyl group is also applicable in the case of brominated compounds but as with the bromine-free compounds a negative result does not necessarily mean absence of *O*-hydroxy-carbonyl group. Negative results are obtained more often when bromine is present than in its absence.

The authors wish to express their thanks to Professor T. R. Seshadri for valuable help rendered in the course of this investigation.

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EFFECT OF ELECTRIC FIELD ON TYNDALL SCATTERING

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Introduction

Amongst the agencies which can bring about a preferential orientation of particles in a mobile colloidal system having anisotropic particles are (*a*) its flow, (*b*) the magnetic field, and (*c*) the electric field. The existence of such orientation has been proved by the work of earlier investigators on double refraction, induced by these agencies.[1] The effect of the preferential orientation on the intensity of Tyndall scattering is of great interest. The only investigations which have been carried out in this field are by (*a*) Freundlich[2] on the changes in Tyndall intensity, induced by flow and (*b*) R. S. Krishnan[3] on the effect of magnetic field on the Tyndall intensity. The effect of the electric field however, has so far received little attention. Mueller[4] attempted to study this effect with bentonite sols, but did not get any positive results. This is probably due to the fact that the particles in the sols used by Mueller were very fine and the orientation was not sufficiently intense to show the effect, owing to the lively Brownian movement of the fine particles. The small intensity of the scattered light might have added to the difficulty in observing the effect. The present investigation was undertaken with a view to study the effect of the electric field on a few typical sols.

Experimental

1. *Preparation of silver iodide sol.*—Silver iodide sol was prepared by the method of Kruyt and Verwey.[5] Silver nitrate was run dropwise into a solution of potassium iodide containing a 10% excess of the latter. The concentrations of potassium iodide solution and silver nitrate solution were so adjusted that the resulting sol contained about 40 millimols of AgI/litre. The sol was then subjected to hot dialysis, until the dialysate gave no test for iodide (14 hrs.). By this method a highly purified sol stabilised by iodide ions and having H^+ as gegen ions was got. It was found advantageous to further stabilize the sol by addition of potassium iodide to give a concentration of 0·001 N iodide ion. The sol was then centrifuged (1800 r.p.m.) for one and a half hours to remove the bigger particles. The clear sol was decanted out. The sol prepared in this way was stable for many months.

2. *Preparation of stearic acid sol.*—Stearic acid sol was prepared by Mukherjee's method.[6] 2·5 gm. of "extra pure" stearic acid was dissolved in 200 c.c. of methyl alcohol. The alcoholic solution was poured dropwise into 700 c.c. of boiling distilled water. Then the excess of methyl alcohol was boiled off. The sol was then filtered through Whatman No. 3 filter-paper, in order to free it from the larger particles. It was then protected by using 0·0003 N sodium hydroxide. The sol prepared by this method was stable for many months.

3. *Sol of Benzopurpurine 6 B.*—A five-year old sol of benzopurpurine (·0002 M) prepared by Doss[7] was used.

4. *Determination of size of the particles.*—The size of the particles in these sols was determined with the aid of the slit-ultramicroscope (Bausch and Lomb). The field of view in the ultramicroscope was limited by using an Ehrlich stop. The dimensions of the Ehrlich stop were determined by means of an eye-piece micrometer, previously calibrated using a stage micrometer. A concentrated sol was put into the cell, provided for the purpose. The slit was turned to the vertical position and the width of the beam as seen in the ultramicroscope was suitably adjusted, by rotating the screw head. This gave the depth of illumination, for the horizontal position of the slit. Then the slit was rotated to the horizontal direction. The volume of the illuminated portion of the sol = Length of the Ehrlich stop × Breadth of the Ehrlich stop × depth of illumination.

The illuminated zone was 0·1 cm. below the surface of the liquid in the cell. The Perrin distribution of micelles did not therefore interfere with the measurements.

The sol was diluted sufficiently so as to give an easily countable number of particles in the small illuminated element of volume. The number of particles N, in the element of volume, was counted every two seconds. About three hundred readings for N were taken. One of the typical sets obtained is given in Table I.

TABLE I

2	2	2	2	2	2	2	2	2	2	2	0	0	0	0	2	2	1	2	2	2	3	3	3
2	3	1	2	3	4	4	2	3	3	4	1	3	4	3	3	2	1	2	0	1	2	2	
0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0	1	2	4	3	4	5	
2	2	1	4	1	2	3	3	3	4	4	3	1	2	3	2	1	1	1	1	0	0	0	
0	1	1	2	1	1	1	0	0	0	0	1	2	2	1	3	2	3	1	1	2	2		
2	2	1	1	2	1	2	1	1	1	2	1	1	1	1	1	0	2	1	2	1	0	2	1
2	2	3	3	3	2	4	1	1	1	2	3	3	4	4	5	0	0	1	3	3	0	1	2

The average of the values was 1·66.

With a view to find out whether the values really correspond to the spontaneous concentration fluctuations, V. Smoluchowski's relations[8] for (*a*) the mean relative fluctuation δ, (*b*) the mean square relative fluctuation δ^2 and (*c*) the probability P (*n*) for the occurrence of any particular N were verified. Results are given in Tables II and III.

TABLE II

$\bar{\delta}_{obs.}$	$\bar{\delta}_{calc.} = 2e^{-\nu}\,\nu k/k\,!$	$\bar{\delta}^2_{obs.}$	$\bar{\delta}^2_{calc.} = \frac{1}{\nu}$
0·66	0·63	0·56	0·60

TABLE III

	$n=0$	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$
$P(n)_{calc.} = \frac{e^{-\nu}\cdot\nu^n}{n\,!}$	31·2	51·77	42·95	23·75	9·85	3·27
$P(n)_{obs.}$	35·0	41·00	46·00	25·00	12·00	2·0

These results (Tables II and III) show that the values for the spontaneous concentration fluctuations obey the Smoluchowski's equations.

The results obtained for the concentration and particle size are given below [Table III (*a*)]:—

TABLE III (*a*)

Sol.	Conc. of sol.	Dilution (to give a countable no. of particles)	No. of particles per c.c. of conc. sol.	Equivalent spherical diameter
Silver iodide sol.	0·25%	1 : 200,000	$7·32\times10^{11}$	104·8 $m\mu$
Stearic acid sol.	0·085%	1 : 10,000	$3·2\times10^{10}$	390·8 $m\mu$

Size of the particles in benzopurpurine 6 B sols however, could not be determined, since (*a*) the sols had, as was to be expected, particles of largely varying sizes and (*b*) the bigger particles broke down on dilution into particles of smaller size.

5. *Shape of the particles.*—Stearic acid sol at temperatures below the melting point has been shown to consist of anisotropic particles by Schlierung experiments.[9] The particles also exhibit in a striking manner the twinkling effect under the ultramicroscope. The sol also exhibits electric double refraction. The quantitative measurement of the double

refraction is difficult since the large scattering in the forward direction interferes with the measurement. These effects disappear when the sol is heated to about 70° C. (a temperature which is higher than the melting point of stearic acid), showing thereby that the observed effects are connected with the anisotropic shape of the particles. In order to find out if the particles are to be considered as rods or discs, the elegant new technique of Langmuir[10] was adopted. In this technique the sol is allowed to flow through a pipette. The stem of the pipette is illuminated by a beam of light polarised at 45° to the direction of flow. The light transmitted by the stem (in which the flow is occurring) is viewed through another polaroid which is crossed with reference to the former polaroid. If the sol consists of rods, the flow of the sol produces a uniform brightening throughout the thickness of the stem of the pipette. If the sol contains discs, a flowing sol shows a central dark band. We have confirmed the observation of Langmuir that vanadium pentoxide shows a uniform brightening. With stearic acid sols a clear dark band is noticed, showing that it contains disc-shaped particles.

Silver iodide sol did not show any schlierung. Under the ultramicroscope, the twinkling was not marked. The Langmuir technique showed that the particles were not appreciably anisometric.

The aged benzopurpurine sol showed marked schlierung. The Langmuir technique with a concentrated sol indicated that the particles were rod-shaped.

6. *Technique for investigating the effect of electric field on Tyndall scattering.*—The electric field was applied by employing platinum or carbon sheet electrodes having apertures in them so as to allow the incident or scattered beam to pass. The light was incident on the sol horizontally. The scattered light was viewed transversely in the vertical and in the horizontal directions. It can be shown that one of the directions of observation can be dispensed with since each of the cases in the vertical direction of observation has a completely corresponding position in the horizontal direction of observation. This fact was also confirmed experimentally. Only the results got with the horizontal direction of observation have been given in Table IV. The field could be applied (*a*) longitudinally parallel to the beam (E_l) or transversely in the vertical (E_v) or horizontal (E_h) directions. These gave six modes of observation. The incident light was polarised horizontally or vertically by using a polaroid. The scattered light was viewed through a polaroid so as to enable us to notice the changes in the intensity of the scattered component, parallel or perpendicular to the direction of the incident

beam. The results are represented in Table IV. The fields used were of the order of 100 volts/cm. D.C. or 220 volts/cm. A.C. Both the types of fields gave identical results. With direct current, however, electrolysis often interfered with the work.

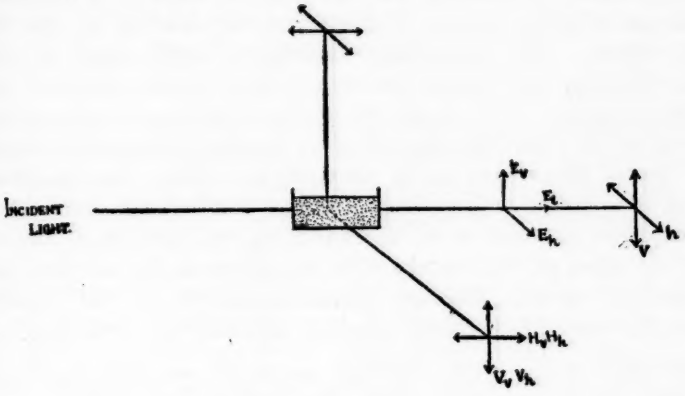

FIG. 1

The various symbols used in Table IV are illustrated in Fig. 1.

TABLE IV

Effect of electric field on Tyndall scattering by stearic acid sol

++ indicates strong brightening on applying the field
\+ indicates moderate brightening on applying the field
– indicates darkening on applying the field

Field	Corresponding Orientation	Effect of the field			
		V_v	H_v	V_h	H_h
E_v		++	+	+	++
E_l		–	–	–	–
E_h		–	–	–	–

The results obtained with benzopurpurine sol were identical with those got with the stearic acid sol. With silver iodide sol, the effects were not observable at the low fields used.

Discussion

Freundlich[11] has proposed a theory to account for the effect of flow on Tyndall scattering which can be applied *mutatis mutandis* to the action of the electric field. He assumes that the scattered intensity is determined by the orientation of the particle in relation to the direction of the incident electric vector. His predictions, no doubt, apply only to positively double refracting rod-shaped particles. This theory however can be extended to apply even to negatively double refracting disc-shaped particles and leads to the result that the scattering intensity will similarly be affected by the electric field in any of the transverse directions. But this conclusion is not at all in accord with our observations. Furthermore, since the scattering intensity is assumed to be dependent on the direction of the incident vector, the effect of field should differ according as the incident vector is horizontal or vertical. This too is not supported by our experimental results. The Freundlich theory therefore breaks down completely.

The applicability of the Rayleigh theory of scattering to the present case may now be considered. The electric field itself tends to orient the particles so as to make their longest axis parallel to the field. We shall discuss how this orientation affects the various scattered components. (In the present discussion we shall assume that the particles are discs.)

The component V_v.—The change in the intensity of V_v can be calculated by finding out the change in the average polarisability of the particle in the verticle direction brought about by the orientating influence of the field. Let the three principal polarisabilites of the disc-shaped particle be a, a and b ($b \ll a$). The average polarisability for the present purposes can be calculated by taking the mean of the values for the extreme orientations of the particle. This comes out to be:

$$\frac{a + \frac{a+b}{2} + \frac{a+b}{2}}{3} = \frac{2a+b}{3}.$$

Particles oriented by E_v would have the various orientations given in Table IV. The average polarisability in the vertical direction corresponding to this orientation would be a. Since a is greater than $\frac{2a+b}{3}$, one should get a brightening in this case. For particles oriented by E_l and E_h, the average polarisability would be $\frac{a+b}{2}$. Since $\frac{a+b}{2}$ is smaller than $\frac{2a+b}{3}$, there would be a darkening in these cases.

The component H_v.—Let the incident light be parallel to the X-axis, the horizontal direction of observation be along Y-axis and let the third axis be the Z-axis. In predicting the action of the electric field we shall consider the three main types of orientation:—

(*a*) The plane of the discs ‖ to the X-axis.

(*b*) The plane of the discs ‖ to the Y-axis.

(*c*) The plane of the discs ‖ to the Z-axis.

In the absence of the field all the three orientations are equally probable. Of these, the orientations corresponding to (*b*) are the only ones which give rise to the component H_v. This type of orientation is favoured by E_h and disfavoured by E_v and E_l. Thus there should be a brightening produced by E_h and darkening by E_v and E_l.

The component V_h.—This component is got only by the orientation (*a*). Since E_l favours this orientation and the other two fields disfavour it, we should expect a brightening with E_l and darkening with E_h and E_v.

The component H_h.—This component is got only by the orientation (*c*). Since E_v favours this orientation and the other two disfavour it, we should expect a brightening with E_v and darkening with E_h and E_l.

The above predictions are summarised in Table V.

TABLE V

Predictions on the basis of the Rayleigh Theory

Field	V_v	H_v	V_h	H_h
E_v	+	−	−	+
E_l	−	−	+	−
E_h	−	+	−	−

A comparison of Tables IV and V shows that the Rayleigh theory is not applicable to the present case.* This is not very surprising. For, the stearic acid sol used in the present work consists of particles which are too large for the Rayleigh theory to hold good. This is supported by the fact that this sol shows a marked Krishnan effect, the ρ_h deviating appreciably from 100%.[12] Moreover, the scattering is highly asymmetric there being a large scattering in the forward direction and the Tyndall light has hardly any preponderance of the blue tint. A rigorous theoretical treatment of

* We have assumed that the particles are disc-shaped. Assuming any other shape does not remove the difficulty.

systems such as this, composed of large and anisotropic particles is beset with many difficulties. Under these circumstances, we would formulate an empirical generalisation, which we would refer to as " The Reflection Rule ", which summarises all the facts observed in such systems:—

" Large disc-shaped or rod-like particles oriented by a linear field, show enhanced scattering when the field is put on, if the plane of incidence and observation is perpendicular to the field; in other orientations the scattering is decreased by the field."

We may also add that the brightening when it occurs, is more marked with V_v and H_h than H_v and V_h.

It was also found that in the brightening positions the H_v or V_h had a distinct red tinge whereas the V_v and H_h had a distinct blue colour. This interesting observation remains to be elucidated.

It is interesting to note that benzopurpurine sol gave the same general results as given in Table I, though this sol consists of rod-shaped particles as shown by the Langmuir technique. We would also like to record the observation that the benzopurpurine sol treated with small amounts of sodium hexa-metaphosphate showed (*a*) diminished scattering and (*b*) no schlierung, and did not show any change in Tyndall scattering when an electric field was applied. This was presumably due to the dispersion caused by sodium hexa-metaphosphate. The exact mechanism of the action of the latter is not clear.

An attempt was made to make similar observations on the effect of flow on Tyndall scattering. Stearic acid sol was allowed to flow in a tube of circular cross-section. The observations were confined to the middle of the tube. A comparison of these observations with those obtained with the electric field, showed that an electric field is equivalent to a flow in a tube (of circular section) in the direction of the field. This is in agreement with the orientation of particles postulated by Langmuir.[10]

It is to be noted that the observations made by R. S. Krishnan[3] on graphite sols, using magnetic fields can mostly be interpreted in terms of the Reflection rules formulated in the present paper.

Conclusion

The study of the action of an electric field on the scattering intensity of sols has thus led to interesting results. The study is useful in determining the shape of the particles. The present technique would be supplementary to the studies of double refraction, in that the latter cannot be conveniently

investigated in a highly scattering system. With slightly conducting sols, large fields can be used so as to produce saturation effects. Under such conditions, the use of rotating fields would bring about a unique orientation of the discs. A superposition of two A.C. fields of different cycles at right angles to each other would have the same effect as the circular field. The use of elliptical fields would reveal any want of equality of the two axes in the plane of discs of flat particles. The technique itself is simpler than the flow technique. Since there is often a large difference in the dielectric constant between the particles and the medium, the orientation is marked even with small fields, and the electric field is thus more powerful than the magnetic field in bringing about orientation.

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KOMBUR SESHA IYENGAR KUPPUSWAMY IYENGAR IN MEMORIAM

THE sudden death due to pneumonia of Kombur Sesha Iyengar Kuppuswami Iyengar—better known as K. S. K. Iyengar—at Mysore, on 23rd June 1944, marks the loss of one of our distinguished Fellows, and one who was well known in mathematical circles in India. The loss is all the more poignant because his death at the age of 45 is so premature.

Born on 29th August 1899, K. S. K. Iyengar finished his early education in the Government High School, and the Central College, Bangalore, and later went to Madras and joined the Presidency College to study for the Honours Degree Examination. He passed the Honours Examination with distinction in 1920, and noticing his pronounced ability in Mathematics his parents decided to send him to Cambridge to study for the Mathematical Tripos.

But for a short spell of a few months at London where he came in contact with Karl Pearson, K. S. K. Iyengar spent the good part of his stay of nearly five years in Europe in Cambridge itself. He took courses in several branches of pure and applied mathematics but his favourite subject was Analysis, and contact with Littlewood had a profound influence on him. He too was one of the many students who went to Cambridge, and came under the spell of the Hardy-Littlewood tradition. The pioneering work of W. H. Young on sets of points made a great appeal to him, and was responsible for the keen interest he always evinced in point set topology. Continental mathematical work of the time on the theory of functions of a complex variable, especially the work of the German school attracted him so much that he once made a trip to Germany and met Koebe who had by then perfected his uniformisation theory.

After taking a star wranglership at Cambridge he returned to India in 1925, and was soon appointed to the position of the Head of the Department of Mathematics in the University of Mysore, at the Central College, Bangalore, in January 1926. It was largely due to his high standards, energy, and vision that the department was adequately equipped with library and other facilities to keep pace with modern developments. He was largely instrumental in introducing rigour in mathematical teaching in the University, in making provision for teaching several advanced branches, specially theory of functions of a complex variable and real variables and

theories of integration, and in introducing methods of mathematical physics as a compulsory subject for the Honours Courses. In 1930 he was elected a Fellow of the Cambridge Philosophical Society from Trinity Hall. He was also a member of the London, American and Indian Mathematical Societies. He was elected a Fellow of the Academy in 1934. He served on the Boards of Studies, Boards of Examiners, Faculties and Academic Council of his University and several others in India. He was also in charge of the teaching of German in the Science Faculty.

It was only in 1938 that K. S. K. Iyengar started publishing his papers regularly and the bibliography of his published papers contains 20 titles and is appended at the end of this note. The important of these can be classified as follows:—four papers on sequences and series, four on summability and Tauberian theorems, three on normal orthogonal sets, two on derivatives of a function, one on integral functions, three on a geometrical problem, and one on the mathematical aspect of the Bhabha-Heitler cascade theory of cosmic rays. One of the papers on derivatives which consists of generalisations of the theorems of Khintchine and Mazurkiewicz were noticed by Saks and published in the *Proceedings of the Warsaw Scientific Society*. The papers dealing with summability are characteristic of his zeal for generalisation and contain many well-known theorems of Hardy and Littlewood as particular cases. The three connected papers on linear transformations of bounded sequences offer a penetrating study of this topic. I shall however give it as my personal opinion that K. S. K.'s paper dealing with the exact solution of the equations of the general cascade theory is his best. This paper, which arose out of discussions with Bhabha on the subject, consists of rigorous proofs for the existence of solutions of a type of differential equations, and the sharp and manifold analytical tools employed serve to show that their author is an analyst of high calibre.

He married in 1926, but had no children. A tall and arresting personality, a good sportsman, a charming conversationalist, full of foibles and lovable just because of them, K. S. K. Iyengar made a deep impression on all who came in contact with him. He was recently getting himself interested in point set topology which he had been studying deeply, but deeper still was his interest in Indian Philosophy, the Bhagavad Gita, Buddhism, religious mysticism, and systems of Yoga. His sudden death removes from our midst a good teacher, and a great friend of all who teach or learn mathematics.

K. S. K. IYENGAR

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